

The University of Chicago

STUDIES IN SPECTROCHEMICAL ANALYSIS

A DISSERTATION SUBMITTED TO THE FACULTY OF THE
DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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The writer wishes to express his appreciation to the J. T. Baker Company for the 1939-40 Fellowship in Analytical Chemistry, to Dr. W. C. Pierce for his unfailing encouragement and suggestions, and to his father and Mr. Kittel for their ever-helpful technical guidance.



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INTRODUCTION

A survey of the literature of spectrochemical analysis shows that the practice of the various workers in the field differs chiefly with respect to the modes of exciting the samples, and the methods of treating the photometric data. Accordingly, the present investigations in these phases of spectrochemical analysis were undertaken.

The excitation sources commonly used are: (1) the direct current (d.c.) arc, (2) the alternating current (a.c.) arc, (3) the spark, and (4) the Lundegardh flame.

Various sources are claimed to have particular advantages, and the beginner may well be confused by the number of different sources and the conflicting claims made for each. Because of these divergent opinions, an attempt was made to gain an understanding of the principles involved in the various electrical excitation methods, to determine the optimum operating conditions for each of the sources, and to classify the kinds of analysis to which each source is best suited. Attention was focussed upon the arc and spark sources, since lack of time prevented any study of flame excitation methods.

The second part of the dissertation deals with another phase of spectrochemical analysis in which an almost equally great variation in opinion and practice exists--namely, the method of determining light intensities by means of the photographic plate.

CHAPTER I

ILLUMINATION SYSTEMS

Before beginning the study of excitation sources it was necessary to decide upon the illumination system to be used, since the arrangement and stability of this system have an important bearing on the reproducibility and accuracy of any spectrographic method of analysis. The following considerations apply to both the Littrow and Cornu types of spectrograph.

1) The spectrograph should be attached to a rigid optical bench. All accessories such as lenses, masks, and sectors should be so mounted that adjustment is easy. When their proper positions have been determined, they should be securely clamped to the bench so that their adjustment is permanent. An unstable optical system prevents the attainment of reproducible spectrum line densities; experience shows that the more nearly line densities can be made reproducible, the more constant are relative intensities of these lines.

2) The most reproducible type of illumination which insures the maximum use of source light is that in which a single condensing lens, placed between the source and the slit, forms an image of the source on the collimating lens of the spectrograph. Since the slit is then uniformly illuminated, the resulting spectral lines are uniformly dense from top to bottom. This simple optical arrangement is not, however, suited to analyses by means of the d.c. arc with carbon electrodes, since the continuous light emitted by the incandescent electrodes produces an undesirable spectrum background. This continuous light may be screened out by a mask in front of the spectrograph prism; the image of the glowing electrodes is thereby occluded. The permissible enlargement of the source image on the collimator lens of the spectrograph is fixed by the diameter of that lens or by the diameter of the apertures in such masks as are used before it. This enlargement is determined by the ratio LC/SL (Figure 1). The distance between the collimator lens and the source is determined by the sum of the focal length of the collimator lens and the length of

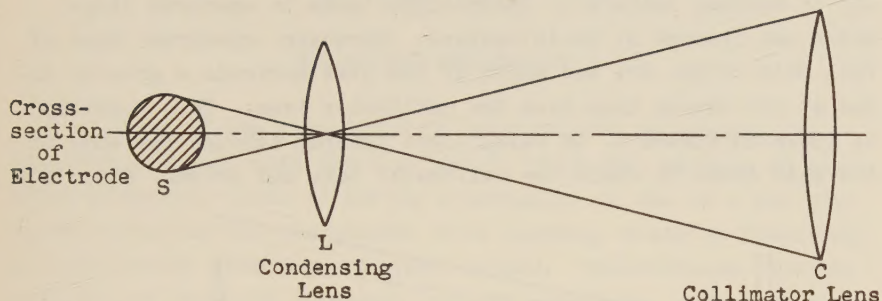


Fig. 1.--Magnification of source image on collimator lens.

the optical bench. Under these conditions, the focal length of the condensing lens is fixed. Its value is readily calculated as follows:

Suppose the electrode diameter is 6 mm., and the aperture of the collimator lens is 75 mm. Then, the distances SL : LC are as 1 : 12.5. If the focal length of the collimator lens is 140 cm., then $SL = 140/12.5 = 11.2$ cm.

When the above values are substituted in the lens equation:

$$\frac{1}{SL} + \frac{1}{LC} = \frac{1}{f}$$

the focal length of the condensing lens is 10.4 cm. In practice, a condensing lens of 10 cm. focal length would be used so that the electrode image on the collimator lens would be 78.5 mm. instead of the maximum desirable 75 mm. It must be remembered that this focal length of the lens is for a particular wave-length. The spectroscopist must bear in mind that the index of refraction of quartz increases as the wave-length diminishes; i.e., the focal length of a quartz lens decreases with diminishing wave-length. If the collimator is also employed as the camera lens (as in the auto-focussing type of spectrograph), the necessary adjustments may be made with the aid of visible light and the collimator lens set for the visible range. When the collimator lens is re-set to photograph the ultra-violet range, the ultra-violet image of the source will be approximately focussed upon it.

An illumination system as reproducible as the one just described may be constructed without a condensing lens between the

source and the slit. The source must be sufficiently far removed from the slit so that the latter is uniformly illuminated from top to bottom; failure to insure this leads to spectrum lines which are densest at their centers. Moreover, spectrum lines of full slit height are too short if the slit subtends a greater angle at the source than does the collimator lens. This condition is shown in Figure 2, in which light passing through the ends of the slit fails to reach the collimator lens and prism. Since the

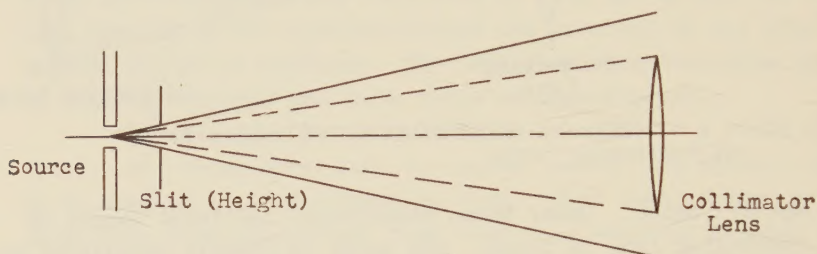


Fig. 2.--Failure of collimator lens to receive light from ends of slit when source-slit distance is too small.

apparatus with no condensing lens fails to make the fullest use of the light emitted by the source, it is less satisfactory for the determination of small traces of elements. Where extreme sensitivity of the spectrograph is not demanded, illumination without a lens is quite satisfactory.

The use of multi-lens optical systems is not usually necessary in quantitative spectrographic analysis. Although the Simeon-Twyman¹ lens arrangement is recommended for qualitative analyses by means of the d.c. arc, it is not commonly employed in quantitative work, because its only advantage--the occlusion of continuous light from the incandescent electrodes--is more easily obtained by the use of a single condensing lens and a mask before the collimator lens.

¹F. Twyman and F. Simeon, Trans. Opt. Soc., 31, 179 (1929-30).

CHAPTER II

THE DIRECT CURRENT ARC

Much of the early work in quantitative spectrographic analysis was done with the d.c. arc.² This arc, because of its fixed polarity, tends to strike continually to one or a few preferred spots on the electrodes. This tendency leads to fractional volatilization with its attendant errors. Nevertheless, for the analysis of minerals, glasses, ceramic materials, and other non-conducting solids, the d.c. arc remains the only available source.

The d.c. arc may be operated on either a 110 or 220 volt current. A 220 volt source is preferable, since the voltage drop across the regulating resistance is larger; the fractional variation in the current will be lower for a given variation in the applied voltage when most of the potential drop is across a ballast resistance. The arc operation is therefore stabilized. The potential drop across the arc is usually from 40 to 60 volts when it is operated at 10 amperes. A simple Ohm's Law calculation shows that the ballast resistance should be variable from about 12 to 36 ohms if the current is to be varied from 15 amperes to 5 amperes (220 volt supply voltage). The resistance should be rated at not less than 2700 watts, and should dissipate this amount energy per second without overheating or changing its resistance during operation.

The generally accepted theory of the d.c. arc is qualitatively the following.³ Electrons liberated at the cathode are accelerated through the arc gap by the potential gradient between the electrodes. On striking the anode, the electrons generate heat and liberate positive ions. These positive ions migrate toward the cathode where, due to their high concentration, a large positive space charge is established. Since there is a po-

²O. R. Torres, Ph. D. Dissertation, University of Chicago, 1938.

³L. B. Loeb, "Fundamental Processes of Electrical Discharges in Gases," John Wiley & Sons, New York, 1939, pp. 605-39.

tential drop of about 20 volts across this small charged region, electrons passing through it are highly accelerated. Thus, the seat of the highest excitation in the arc is the region immediately adjoining the cathode.

The fact, discovered by Mannkopf and Peters, that the excitation of higher atomic levels occurs in the immediate neighborhood of the cathode, is of little importance in quantitative spectrographic analysis, since this cathode layer effect disappears when the size of the sample is greater than 3-5 mg. The existence of the cathode-layer effect throws some light on the theory of the d.c. arc, however, so that its discussion is relevant in a consideration of excitation sources and mechanisms. Gerlach⁴ offers three explanations for this effect:

1. Increased excitation of atoms by electron impact in the region of large potential drop, that is, in the cathode layer.
2. Higher temperature in the gas layer of the cathode region.
3. Higher concentration of atoms and ions in the cathode layer.

The first explanation was rejected by Mannkopf, who showed that the effect is still present 3×10^{-4} seconds after the potential is removed. Witte,⁵ on the other hand, attributes the effect to the first-mentioned cause; he bases his opinion on the rapid decline in intensity of Cd: 2749 Å when the potential is cut off. Witte believes that excitation in the region of the cathode is due primarily to electron impact, whereas excitation in the central column of the arc is due to kinetic (thermal) energy. The electronic temperature is much higher than the gas temperature in the cathode region; in the arc column, however, the electronic temperature and the gas temperature differ by only a few per cent because of the low potential gradient.

Gerlach's second explanation has been excluded⁶ on the grounds that band spectra arising in the cathode layer show no evidence of greater molecular dissociation (temperatures may be

⁴W. Gerlach and W. Gerlach, "Die Chemische Emissionsspektalanalyse," II, L. Voss, Leipzig, 1933.

⁵H. Witte, Zeit. für Physik., **88**, 415 (1934).

⁶W. Gerlach and W. Gerlach, op. cit.

calculated from band spectra intensities). Gerlach accepts the third explanation as most likely--namely that the enhanced excitation is due to the greater concentration of atoms and ions in the region immediately adjoining the cathode surface. The ions are drawn to the cathode under the influence of the field, and concentrate in the cathode layer. That the positive ion concentration is a maximum in the cathode layer may be inferred from the large space charge in that region. It therefore seems probable that both the first and third causes are operative in producing the cathode layer effect. The region of favorable excitation which extends one to two millimeters from the cathode surface owes its existence to the higher atomic and ionic concentrations. The increased concentration of atoms in the cathode layer is due to the fact that ions are converted to atoms by recombination with electrons at the cathode surface. A very much narrower region of still greater excitation is found even closer to the cathode; excitation there is attributed to high velocity electron-atom (or ion) collisions. In this zone, the two modes of excitation are probably co-extensive; in the region of favorable excitation (commonly known as the cathode-layer) the enhancement is ascribed to the higher concentration of atoms or ions excited by both electronic and thermal collisions. Finally, since the electronic and kinetic temperatures are practically identical in the central arc column (i.e. all material particles in this part of the arc have reached a condition near equilibrium) it is quite proper to speak of "thermal" excitation in that zone.

The extent of the enhancement of spectral sensitivity in the cathode layer depends upon the concentrations and the ionization potentials of the impurity sought and of the matrix material of the sample. Thus, for example, when the concentration of the impurity is very low, the relative increase in sensitivity in the cathode layer is greater than that in the central arc column. The lower the excitation potential of the impurity, the greater its ionization and the higher its concentration in the cathode layer due to ionic migration under the influence of the field. In general, the cathode layer effect is less pronounced where the ionization potential of the major constituent is low, since under these conditions, ions of the matrix material occur in relatively greater numbers, and take over the function of the positive-current-carriers. Thus, the detection of trace elements is ordinarily

less sensitive in the salts of the alkali metals than in the presence of matrix atoms of higher ionization potential.

As already mentioned, the undesirable feature of the d.c. arc is the fractional volatilization of the sample which results from the tendency of the arc to persist in striking to a few preferred spots on the electrodes. The abreissbogen of Gerlach⁷ was designed to interrupt and rekindle the arc periodically by the mechanical oscillation of one of the electrodes to and from the fixed electrode. The time intervals in which there is no discharge permit the electrodes to cool so that no one spot is preferentially heated and allow the gap to regain its former condition. This modification of the d.c. arc has been employed in the analysis of both metal electrodes and non-conducting solids in craters of carbon electrodes. Although much is claimed for this scheme by its inventor, and although it does strike at the fundamental defect in the d.c. arc, nevertheless it seems to be a rather clumsy solution of the difficulty. Numerous attempts have been made to make the d.c. arc intermittent.⁸ In addition to the mechanically interrupted arcs of Gerlach and Calker, a number of electrically quenched arcs have been described.⁹

An investigation was made by the author of the effect produced by modulating a direct current arc with radio frequency oscillations. The circuit used is shown schematically in Figure 3. A push-pull oscillator operating at 25 watts and employing two R.C.A. UX210 vacuum tubes was inductively coupled to a circuit fed by a 220 volt d.c. generator. The broadcast coil consisted of 25 or 50 turns of wire wound on the outside of a 1-liter beaker. The pick-up coil, consisting of 25 turns, was co-axial with the sending coil; variable coupling was obtained by separation of the coils along their common axis. The oscillator frequency was varied from 1000 to 2000 kilocycles by means of the split-stator condenser, C_1 . By varying the condenser, C_3 , between 0 and 0.0015 μ F. the discharge circuit was tuned to resonance with the oscillator. Choke coils were inserted in the d.c. leads to prevent radio frequency leakage into the generator mains. A cathode ray

⁷W. Gerlach and W. Gerlach, op. cit., pp. 3, 48.

⁸A. Schleicher, Zeit. für anal. Chemie, 117, 52 (1939).

⁹K. Pfeilsticker, Z. Elektrochem., 43, 719 (1937);
K. Pfeilsticker, Z. Metallkunde, 30, 211 (1938).

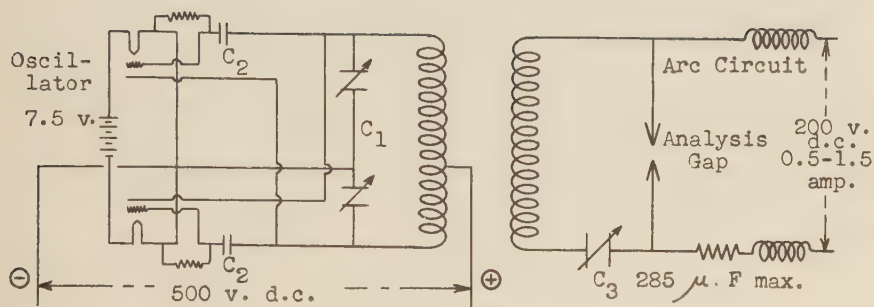


Fig. 3.--Circuit for radio frequency modulation of d.c. arc.

oscilloscope was placed across a portion of a high resistance which spanned the arc gap; the oscilloscope pattern showed the radio frequency oscillations superimposed upon the pattern of the d.c. potential. The source thus obtained yielded spectra which, with regard to sensitivity and reproducibility, were no better than the ordinary d.c. arc spectra obtained with comparable current. To all appearances, the spectra obtained with the two sources were identical.

One of the factors studied in the d.c. arc was the effect of current density. Experience had indicated that as the arc current is increased, the light intensity rises. Such an effect might be attributed either to increased vaporization of the sample or to increased efficiency of excitation. In order to distinguish between the two possibilities, some experiments were made with salt solutions containing small amounts of manganese, lead, tin, aluminum, and zinc in Cholak's synthetic biological ash.¹⁰ A definite volume of this solution (0.050 ml.) was dispensed through a micro-buret into the craters of carbon electrodes which were then carefully dried in an oven. All the samples were arced to the complete disappearance of the sample. It was found that

¹⁰J. Cholak, Ind. Eng. Chem., Anal. Ed., 7, 287 (1935).

the density of the spectral lines increased regularly with increase in the arc current. Since the samples were completely volatilized, the implication is that more efficient excitation prevails in arcs of higher current density. No attempt was made to express the relationship between light intensity and current strength quantitatively, since a microphotometer was not available at the time. Expressed somewhat differently these results indicate that light emission involves two more or less discrete factors: volatilization of the sample, and excitation of the vaporized material. The experiments cited do not preclude the possibility that some excitation and volatilization take place simultaneously.

The d.c. arc, unlike the sources to be subsequently discussed, finds particular application in the analysis of non-conducting solids. Minerals, glasses, abrasives, soils, and ores are but a few of the types of substances which have been satisfactorily analyzed spectrographically by d.c. arc excitation; in general, these substances are poor electrical conductors which cannot easily be made conducting by solution in mineral acids or by fusion with the common fluxes. The samples are usually finely comminuted and mixed with added quantities of a suitable flux; an internal standard is often added, as well. The powdered mixture is placed in the crater of a carbon electrode and arced at a given electrode separation with a suitable current. The most suitable diameter of the electrodes and the optimum depth and diameter of the crater in the carbon anode depend upon the boiling point of the substance to be arced. In general, 3/16" diameter electrodes with craters 1/8" in diameter and 5/16" deep are satisfactory. For the more volatile salts such as stannous chloride, zinc chloride, lead chloride, and cadmium chloride, a somewhat deeper crater is to be preferred. It is convenient to pre-arc the sample until the anode has become hot enough to fuse the sample into a globule; at this point, the carbon anode is removed from its electrode holder and the carbon wall trimmed down to expose the fused globule. If this practice is not employed, much continuous light is produced by the burning of the carbon, and a heavy spectral background results. Some workers¹¹ maintain a constant electrode separation by projecting an image of the arc on a screen and reg-

¹¹M. Slavin, U. S. Bur. Mines, Private communication.

ulating the electrode holders during the arcing so that the electrode images coincide with predetermined marks on the screen. If the flux has been properly chosen, the arc should burn quietly with a characteristic flame color; exhaustion of the sample is marked by hissing of the arc and the appearance of the characteristic blue color of the carbon arc. The use of rotating sectors to prevent over-exposure is to be preferred to stopping the arc before the sample has been completely vaporized.

Some spectroscopists avoid the use of internal standards by weighing the sample on a semi-micro balance and arcing it to exhaustion. This practice in the hands of an experienced operator¹² is said to yield excellent results; it should not be recommended to beginners.

¹²Ibid.

CHAPTER III

THE ALTERNATING CURRENT ARC

If the virtue of the abreissbogen lies in the intermittent nature of its operation, then a similar but much more convenient source should be the alternating current arc. The 220 volt a.c. arc is not self-sustaining at ordinary ampereages, however. Two alternatives are: (1) the high voltage a.c. arc, the voltage of which exceeds the breakdown potential of the gap, and (2) the low voltage a.c. arc periodically ignited by a low power spark.

Although the Flammenbogen has long been used in Germany, it remained for Duffendack¹³ to employ the high voltage a.c. arc as a routine source. His circuit is shown below in Figure 4.

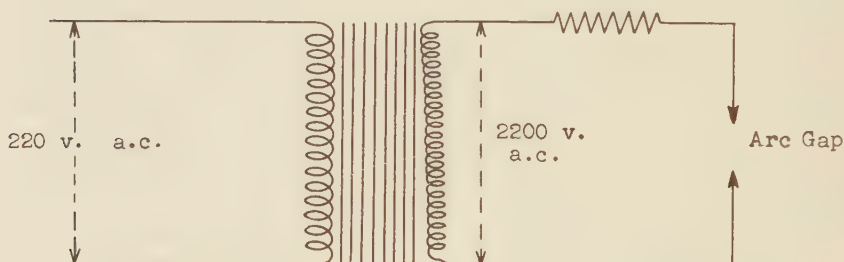


Fig. 4.--Circuit for high voltage a.c. arc

There must be some means of limiting the current drawn by the arc, if large transformers (10 k.v.a.) are used on ordinary current mains. Four possibilities suggest themselves:

1. Impedance control in the primary circuit.
2. Impedance control in the secondary circuit.

¹³O. S. Duffendack and R. Wolfe, Ind. Eng. Chem., Anal. Ed., 10, 161 (1938).

3. Resistance control in the primary circuit.

4. Resistance control in the secondary circuit.

Either (1) or (2) is completely satisfactory. Resistance control of the arc is not as satisfactory, since the energy in excess of that dissipated by the arc appears in the resistances. With an arc operated at 3 amperes on 2200 volts, over 6 kilowatts of energy must be dissipated as heat. In practice it is found that the secondary windings of a 5 k.v.a. transformer serve as an excellent reactance for a 10 k.v.a. transformer, limiting the current in the arc to 1.2 amperes. Higher currents may be obtained if only a portion of the secondary coil of the smaller transformer is employed.

At the beginning of this study it was thought that the excellent results given by the a.c. arc might be due to the high voltages used--i.e. that vaporized sample material in the gap might be efficiently excited by the electron impacts due to the high impressed voltage. In order to gain more insight into the mechanism of this source, it was necessary to study the current-voltage characteristics by means of an oscilloscope. Current oscillograms were obtained by connecting the oscilloscope plate leads across a 10 ohm resistance in series with the arc. Voltage oscillograms were obtained by connecting the oscilloscope plate leads across 5,000 ohms of a 100,000 ohm resistance which spanned the arc gap. The oscillograms are shown in Figure 5. There is no difference in phase between the current and the voltage, regardless of whether the current is controlled by impedance or by resistance.

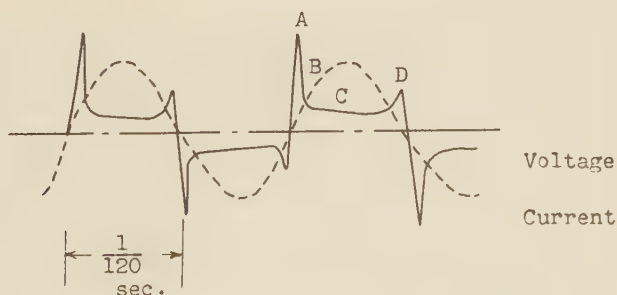


Fig. 5.--Current and voltage oscillograms of the a.c. arc

The voltage oscillogram is characterized by four distinct regions in its cycle. The voltage first rises until the breakdown potential of the gap is reached (A). The magnitude of this breakdown voltage is about 1400 volts for an electrode separation of 0.5 mm.; it increases to about 1800 volts when the separation is increased to 5 mm. When the breakdown potential of the gap is reached, the air between the electrodes becomes conductive, and the discharge passes into a transitory glow discharge (B) marked by a fall in the potential. The duration of the glow discharge depends upon the nature of the surface of the electrode material. Substances which, like iron,¹⁴ form a heavy oxide coating in the arc, extend the life of the glow discharge period. The arc between carbon electrodes, on the other hand, has only a fleeting glow discharge interval. This difference is shown in Figure 6.

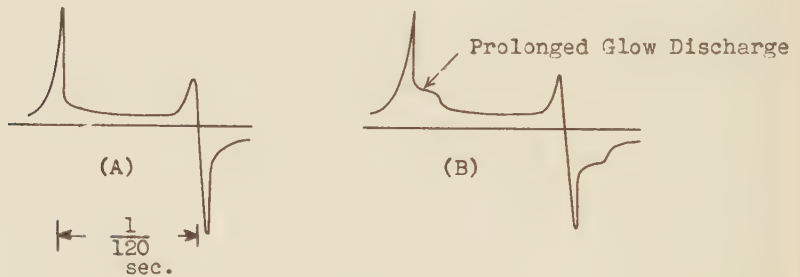


Fig. 6.--Voltage oscillograms for (A) carbon arc and (B) iron arc.

The third phase of the voltage cycle (C, Figure 5) is a period of long duration in which the arc voltage remains nearly constant at about 50 volts. In this phase, the a.c. arc is, to all intents and purposes, merely a d.c. arc. The final rise of the potential (D) marks the last stage in the voltage cycle of the arc. As the current falls off, the number of ions in the gap decreases; since the resistance of the gap is thereby increased, the voltage rises, but not to its initial high value, since the potential across the transformer secondary has dropped by this time. The surge of the voltage at the end of the cycle is, in

¹⁴H. Vincent and R. Sawyer, J. Appl. Phys., 8, 163 (1937).

other words, merely another indication of the "negative characteristic" of all arcs--the fact that the current and voltage vary in inverse ratio rather than in accordance with Ohm's Law.

As a corollary to the study of the current and voltage characteristics of the a.c. arc, the relation between the phase of the current or voltage and the emission of light was investigated. A sector was constructed with eight holes cut on a spiral; the holes were on radii separated from each other by 22.5° . The sector was mounted on the shaft of a synchronous motor so that the uppermost hole revealed the slit to the arc when the phase of the current was 0° . The remaining holes passed before successively lower portions of the slit when the phase of the current was 22.5° , 45° , 67.5° , 90° , etc. The fact that the primary and secondary transformer currents are nearly 180° out of phase is of no consequence, since the sign of the current does not affect the argument; the positive and negative parts of the cycle are equivalent.

The interesting, although perhaps not surprising, result of the experiment just described is that light emission is a maximum for maximum current. The light emission thus parallels the current density in the arc. It might have been predicted that the maximum light emission, and the emission of light from higher atomic or ionic energy levels, would occur during the breakdown of the potential or during the glow discharge interval. The failure to find a maximum in these intervals indicates that the excitation processes in the a.c. arc are linked with the density of the electron stream, rather than with the potential which accelerates the electrons.

The existence of the cathode layer effect in the a.c. arc shows in yet another way the similarity between this and the d.c. arc. The effect is easily demonstrated by focussing an enlarged image of the arc on the slit of the spectrograph. The spectrum lines are enhanced in the region of the arc immediately adjacent to each electrode. If dissimilar electrodes, such as carbon and zinc, are employed, the zinc lines are enhanced in the regions of the arc adjoining both the carbon and the zinc electrodes. Each electrode behaves as a cathode every $1/120$ th of a second in the a.c. arc. Apparently, the zinc ions are drawn to the carbon electrode while it is the cathode and emit their radiation in its erstwhile cathode region.

Duffendack¹⁵ has stressed the importance of maintaining a fixed electrode separation in the a.c. arc; he has shown the variations in line intensity ratios which may be expected when the electrode separation is changed. The effect is ordinarily attributed to changes in the arc temperature or in the field configuration when the gap is widened. The writer has accumulated some evidence which indicates that the variations may be due to changes in the path of the light and, in certain instances, to variations in spectrum background. Doubtless, variations in gap width do involve changes in arc temperature which in turn affect the intensity ratios. That another cause may also be operative is deduced from the following observations.

As the electrode separation was increased by moving both electrodes away from the optical axis the lines diminished in intensity and finally disappeared entirely, leaving only the band spectrum of the N_2^+ molecule-ion and the continuum present in all carbon arcs. On the other hand, when the electrode separation was increased by moving only one electrode away from the optical axis, the diminution in line intensity was much less. Finally, the same observations were made when the same experiments were carried out with the d.c. arc. The effect is therefore not unique to the a.c. arc, but is rather to be associated with the optical system. Figure 7 shows the solid angles through which light is emitted from the gap for two different electrode separations.

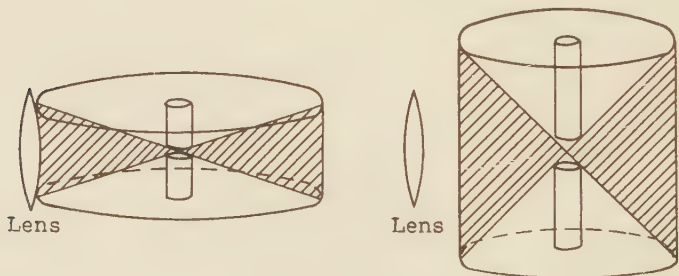


Fig. 7.--Variations in solid angle of light emission with electrode separation.

¹⁵O. S. Duffendack, op. cit.

It is evident that a greater fraction of the total light emitted will reach the spectrograph slit, regardless of whether or not a condensing lens is used, when the electrode separation is small. As the electrode separation is increased, the light is emitted over a much larger solid angle, so that a smaller fraction of it passes into the spectrograph. Much of the light emitted from the long arc is not line radiation, however; it consists largely of the band spectrum of N_2^+ ions, since these ions take over the function of current-carriers when the sample ions are so reduced in concentration in the arc as to be inadequate. As the electrode separation is increased, the absolute densities of two lines diminish, while the background remains approximately constant in density. If the two lines are of widely different intensity, or if their backgrounds are appreciably different, their intensity ratio varies when their absolute densities decrease and their backgrounds remain constant. The effect of background is to make a weak line appear too strong as compared with an intense line. Thus, the intensity ratio of a weak line to a strong line in the presence of background increases as the electrode separation is increased--i.e. as both lines are diminished in density. The quantitative variation in intensity ratio for lines of different intensity in the presence of background is treated in the portion of this dissertation dealing with photometric procedure.

The a.c. arc is particularly well suited to the analysis of liquids and solutions which may be dried on the surfaces of flat-topped carbon electrodes. Examples of its use are: the analysis of water- or acid-soluble powders and ores, caustic liquors, and biological material which has been ashed and dissolved. There has also been a trend toward the replacement of the spark by the a.c. arc in the analysis of ferrous metals¹⁶ where speed is desirable. Shorter exposures are made possible by the greater average current density of the a.c. arc. The procedure generally followed in the analysis of solutions is to place a drop of the liquor on the tip of each electrode and to dry the electrodes by placing them in a suitable heater. The drying temperature should be so adjusted that crystal segregation on the surface of the electrode is a minimum; it must of course, be low enough to avoid spattering. The electrodes are then placed in an arc holder of the gen-

¹⁶H. Vincent and R. Sawyer, Metal Progress, 36, 35 (1939).

eral type designed by Duffendack.¹⁷ If the solid is low melting, the use of water-cooled electrode holders is recommended.

It is usually necessary to pre-arc the sample for thirty seconds or so before making the exposure for record. During this pre-arc interval the sample covers the electrodes more uniformly; the electrode separation is adjusted at this time. It is important not to continue the exposure to the point of exhaustion of the sample, since the background caused by N_2^+ ions and incandescent carbon particles increases rapidly toward the end of the exposure. The volume of solution placed on the electrodes is not critical, nor need it be definite, since an internal standard is always added to the solution.

¹⁷O. S. Duffendack and R. Wolfe, op. cit.

CHAPTER IV

THE CONDENSED SPARK

In the high frequency spark, the analytical spectroscopist possesses a source which can be subjected to much wider variations in conditions than are the a.c. or d.c. arcs. The circuit, shown schematically in Figure 8 (commonly called the Feussner circuit), contains the following electrical elements:

1. A transformer, usually rated at about 1 k.w., operating on 110 or 220 volts and delivering 15,000 to 25,000 volts from the secondary.
2. A condenser, variable in fixed steps from 0.001 to 0.006 microfarads.
3. An inductance, variable in steps from 1000 microhenries down to the fixed inductance of the circuit leads.
4. A synchronous interrupter.

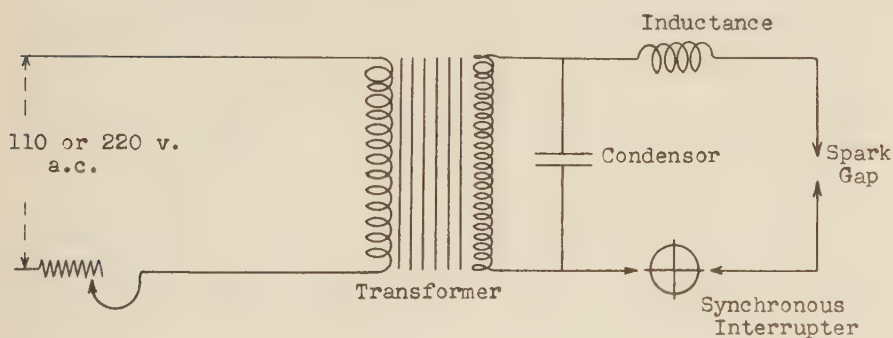


Fig. 8.--Condensed spark circuit

The manner in which variations of the inductance and capacity affect the nature of the discharge will be discussed below. It is now realized that there is no essential difference between the spark and the a.c. arc; in fact the spark appears to be merely a flexible type of high frequency a.c. arc.

The low pressure gas discharge tube serves as a convenient starting-point for developing the mechanism of spark discharges. Suppose that a slowly rising potential be impressed across the electrodes of a gas discharge tube. In the gap the few ever-present electrons and positive ions (produced by radioactive bombardment and cosmic ray action) are accelerated toward the anode and cathode, respectively. Under low potentials the electrons the electrons cannot acquire velocities sufficient to make them collide inelastically with the atoms and molecules encountered. The current flowing under such conditions is aptly called the "saturation current"; the magnitude of this current depends upon the pressure of the ambient gas and the concentration of the radioactively produced ions. As the potential is further increased, the velocity of the ions and electrons increases; the frequency of elastic collisions increases, but the current remains nearly constant. When the potential is raised sufficiently, the electrons acquire sufficient velocities to collide inelastically with atoms and molecules and thus to produce new ions and electrons. This process of ionization by collision, once initiated, is cumulative, and grows in a sort of geometric progression.

When the avalanche of current-carriers reaches a certain critical stage, the resistance of the gap is said to be broken down, and a luminous discharge occurs in the tube. The potential at which this breakdown occurs is called the "critical breakdown potential" of the gas; it is a function of the particular gas in question, the pressure, the electrode separation, and the shape of the electrodes. The passage of the current at potentials insufficiently high to cause ion-multiplication by collision is termed the "region of dependent discharge," because here the magnitude of the saturation current depends upon the number of ions of radioactive or cosmic ray origin initially present in the gap. The passage of currents greater than the saturation current is termed the "region of independent discharge" because the discharge is independent of the initial concentration of ions in the gap after the process of cumulative ionization has set in.

Like the glow discharge tube, the high frequency spark begins as a dependent discharge but quickly becomes an independent discharge when the potential exceeds the breakdown value.¹⁸ Once

¹⁸L. B. Loeb, op. cit.; J. S. Townsend, "Electricity in Gases," Oxford University Press, Clarendon, 1915.

the spark discharge has set in, its behavior differs completely from that of the glow discharge. The spark discharge takes the form of a high frequency, high current oscillatory arc. The current of electrons through the circuit behaves as though it possessed a kind of inertia, for the condenser is first charged to one potential, and then discharged, not to zero, but to a potential of opposite value. The action of the condenser may be likened to the free oscillations of a coiled spring; the electrical oscillations, like the mechanical oscillations of the spring, are gradually damped by losses of energy, as heat in resistances. Figure 9 shows the course of the potential and current in the spark.¹⁹

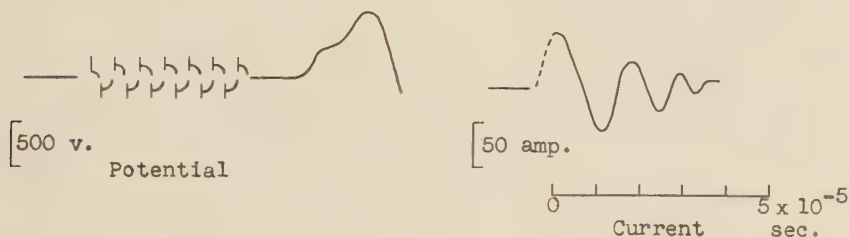


Fig. 9.--Current and voltage oscillograms in the spark (after Kaiser).

It will be noted that the current in the spark follows a damped sine wave, the decrement of which is approximately linear. Moreover, the currents set up in condensed spark discharges may be much higher than those employed in the a.c. or d.c. arcs. These rapid pulsations of high currents excite higher energy levels in the atoms than do the arcs. These high momentary energies in the spark, by ionizing and exciting the atoms, give rise to the so-called "spark" or ion spectrum as well as the "arc" or neutral excited atom spectrum.

Lawrence and Dunnigton²⁰ observed the time order of ap-

¹⁹H. Kaiser and A. Wallraff, Ann. der Physik, **34**, 297 (1939).

²⁰E. O. Lawrence and F. G. Dunnigton, Phys. Rev., **35**, 396 (1930).

pearance of the several kinds of lines found in spark spectra. Using a Kerr cell as a shutter to photograph the spark at various short intervals after the gap breakdown, they found that the order of appearance of lines was as follows: (1) spark lines of air, (2) spark lines of electrode material, and (3) arc lines of electrode material. The first discharge to pass from one electrode to another (the leader spark) ionizes the air, and causes the emission of spark lines of nitrogen and oxygen. When the discharge strikes the opposite electrode, a cloud of luminous metal vapor is released with great velocity. The velocity and direction of the vapor cloud varies with the type of electrode material; in general, the cloud proceeds with a velocity of from 100 to 1000 meters per second. The structure of this vapor cloud appears to be little influenced by the subsequent oscillations of the spark; this fact has been revealed by studies with high velocity rotating mirrors.

In order to investigate the number of spark discharges produced during each half cycle of the transformer primary current, a rotating mirror was constructed according to a design given by Schöntag.²¹ A circular mirror 1 1/2 inches in diameter was mounted on the shaft of a variable-speed motor; this mirror was inclined about 8° from the normal to the shaft. When the shaft rotated, the mirror described a wobbling motion. The image of a series of spark discharges appeared as a number of luminous spots on the circumference of a circle in the image plane of the mirror. Figure 10 shows several of such images of spark discharges obtained with this stroboscope. The mirror speed is so adjusted that each quadrant of the circle represents one-half cycle of current. For each half cycle the number of discharges (each of which is a train of radio frequency oscillations) may range from a few to 15 or 20, depending upon the inductance and capacity of the circuit, the electrode separation, and the nature of the electrode material.

It is well known that low inductance discharges are highly damped; i.e. the condenser discharges its energy in a relatively small number of oscillations per train (discharge). The instantaneous currents in the low inductance discharge are therefore

²¹A. Schöntag, "Beiträge zur quant. Spektralanalyse," Frommhold & Wendler, München, 1936, p. 57.



Fig. 10.--Rotating mirror images of spark discharges

much greater than those in the high inductance spark; as a result, the luminosity of the low inductance discharge is considerably greater. These rotating mirror studies reveal the interesting fact that the number of discharges which may take place within a half cycle is far from constant. The quality and number of the discharges may vary widely and erratically, particularly as the surface of the electrodes becomes pitted or oxidized.

It was in the knowledge of this fact that Feussner²² adapted from radio technique the synchronous spark interrupter which bears his name. In essence, it consists of a set of electrodes so mounted on the shaft of a synchronous motor that a spark train passes between them and a set of fixed electrodes once in each half cycle of current. The position of the fixed electrodes is so adjusted with respect to the rotating electrodes that this spark train passes when the potential across the transformer secondary is a maximum. The condenser in the discharge circuit is thereby fully charged once in each half cycle, and the number of discharges across the analysis gap is limited to one per half cycle. The experience of the writer and other workers who have constructed such synchronous interrupters bears out the claims of constancy made for this source.

Even though, by use of the Feussner circuit, the spark is limited to one discharge per half cycle, there remain several factors which may be varied to alter the nature of the discharge.

²²O. Feussner, Archiv. für Eisenhüttenwesen, 6, 551 (1933).

Several considerations govern the choice of the inductance and capacity to be used:

1. The condensor must be of sufficient capacity to store up all the energy made available to it by the transformer secondary without rupture of its dielectric or causing a spark to jump across the safety gap of the transformer.
2. The inductance must be high enough to suppress the background of continuous radiation which appears in low inductance spark discharges.
3. The inductance should be low enough to preserve the high current density of the spark. The higher the inductance, the lower the current in the discharge. A counter-e.m.f. set up in the inductance opposes the forward-e.m.f. and the current associated with it. Ordinarily, an inductance of 20 to 1000 micro-henries is employed.
4. The amount of energy employed (determined by the rating of the transformer, and the magnitudes of the inductance and capacity) depends upon the particular metal under analysis. Thus, ferrous alloys will withstand the action of a high power spark without melting; lead samples must be sparked by a relatively low power source.

It is convenient to discuss the two extreme types of discharge attainable with the circuit described, realizing that all intermediate types of discharges are possible. These two types are those obtained with high and low inductance. The low inductance discharge is commonly known as the "cold" spark, although the currents flowing in it may be many times as great as those in the high inductance or "hot" spark. The low inductance spark differs outwardly from the high inductance spark in several respects:

1. It is more luminous; usually it is bluer in color.
2. It is noticeably louder and more explosive.
3. Although higher currents pass, less electrode material is volatilized.

More important to the spectroscopist than these superficial differences are the differences in the spectra of the two sources:

1. The "cold" spark gives a heavy uniform background of

continuous light. Presumably, this background of continuum is due to electron radiation in a field of positive ions.²³ On the classical model of the atom, it is pictured as resulting from energy released by electron transitions between hyperbolic orbits. Electrons passing close to positive ions release some of their kinetic energy as light energy and pass on without being captured by the ions.

2. Since the spectra of low inductance sparks contain many more spark lines of the electrode material, higher energy transitions are here at hand.
3. Lines due to ionized oxygen and nitrogen atoms are found in the spectra of low inductance sparks. They are usually completely absent from the spectra of high inductance sparks.
4. The surface of the electrodes in a low inductance spark is relatively smooth, whereas numerous pits and tiny metallic globules cover the surface of the electrodes in a high inductance discharge.

The fact, mentioned above, that less electrode material is volatilized in the low inductance spark deserves further attention, since the currents in the low inductance spark are greater than those in the other type of spark. To explain this apparent anomaly two functions of the electron stream in the spark must be recognized. In the first place, volatilization is not merely a thermal process in the spark; electrode material apparently is also dislodged by the impingement of high velocity electrons on the metal surface. Secondly, excitation in the spark must occur chiefly by the collision of high-velocity electrons with metal vapor atoms. The rapidly changing direction and velocity of the electrons in the oscillatory discharge under the influence of the rapidly alternating field forbid a condition of thermodynamic equilibrium involving atoms, ions, and electrons. To speak of "thermal" excitation in the spark is therefore meaningless, since the very concept of temperature is based upon gas kinetic equilibrium.

²³W. Finkelburg, "Kontinuerliche Spektren," Springer, Berlin, 1938, p. 300; W. Finkelburg, *Phys. Rev.*, 45, 341 (1934); W. Finkelburg, *Zeit. für Physik*, 88, 247 (1934).

Since the low inductance spark is highly damped, by the time the electrodes have been heated enough to permit thermal vaporization, the spark has been extinguished. The duration of the cold spark may be only 1/10,000th of a second, and the electrodes cool in the non-discharging interval of 1/120th of a second which follows. Schöntag²⁴ gives the equation:

$$Q/F = (T_1 - T_2) \cdot z \cdot \alpha + k \cdot (T_1^4 - T_2^4) \cdot z, \quad ,$$

in which Q/F is the heat transmitted to the electrodes per unit area, $T_1 - T_2$ the temperature difference between the electrodes and the surroundings, z the duration of the spark, and α the specific heat of the electrodes. The large z factor in the high inductance discharge outweighs the higher temperature difference $T_1 - T_2$ in the low inductance discharge, with the result that Q/F is greater for the high inductance spark. Since the heat transmitted to the electrodes is greater in the high inductance discharge, more of the sample is vaporized.

The mechanism of the spark given above is a qualitative one, since the analytical spectroscopist need not inquire into the more intricate details of the process. The works of Kaiser, Loeb, and Townsend already cited are recommended to those desiring information on these points.

The spark finds its greatest application in the analysis of alloys; aluminum, copper, magnesium, nickel, zinc, iron, and the many alloys of these metals are currently analyzed by means of spark excitation. The accuracy attainable in these analyses is usually much higher than that attainable by use of arc sources, chiefly because of the high degree of constancy of the Feussner spark circuit discharge; in the most careful work, average deviations are usually within ± 3 per cent of the correct value.²⁵ In the a.c. arc, average deviations of ± 5 per cent, with occasional variations of over 10 per cent are considered excellent. The limiting factor in accuracy and precision in spark methods is usually not the inconstancy of the source, but rather the inhomogeneity of the alloy and the errors connected with the photographic process.

The form of the electrodes is usually cylindrical, with a

²⁴H. Vincent and R. Sawyer, Metal Progress, 36, 35 (1939).

²⁵Ibid.

low cone ground or cut on the surface to be sparked; ordinarily, the alloy is cast in the form of pins. The amount of self-inductance and capacity to be employed in the discharge circuit, as well as the maximum power used, depend upon the nature of the metal to be analyzed. These factors are varied separately, until a combination is obtained which leads to satisfactory sensitivity of detection and maximum reproducibility in the intensity ratios of the lines used for analysis. The internal standard line must ordinarily be one in the spectrum of the alloy matrix, since it is not feasible to add a foreign substance. Usually it is necessary to submit the electrodes to a preliminary sparking before the record exposure is made in order to condition the surface of the electrodes and obtain reproducible line intensity ratios. During this pre-spark interval the surface of the electrodes may become oxidized or nitridized; until this more or less stable condition is reached, the intensity ratios are likely to vary, eventually approaching an asymptotic limit. The use of an inert atmosphere may hasten the attainment of this steady surface condition and facilitate the attainment of reproducible intensity ratios. Fitz,²⁶ Wagner,²⁷ and Tlapa,²⁸ for example, analyzed lead for bismuth and silver by sparking the lead electrodes in an atmosphere of nitrogen; they report an accuracy and precision greater than those obtainable by the conventional method of sparking in air.

In general, the sensitivity of detection in the spark source is considerably lower than in the a.c. arc. Where the sensitivity of the spark is inadequate, an a.c. arc of suitable power may be employed.

²⁶E. J. Fitz, Master's Dissertation, University of Chicago (1940).

²⁷W. Wagner, Master's Dissertation, University of Chicago (1940).

²⁸C. J. Tlapa, Master's Dissertation, University of Chicago (1941).

CHAPTER V

PHOTOMETRY IN SPECTROCHEMICAL ANALYSIS

Since the photographic plate is widely used for the measurement of radiant energy, the relation between the light intensity and the photographic effect has been very extensively studied.²⁹ Despite this work, however, the spectrochemical analyst must frequently investigate the process in order to establish the validity of his procedures. A survey of the recent literature in the field reveals misconceptions and general lack of agreement as to the most satisfactory method of measuring and treating photometric quantities.

The following definitions and symbols are used in the ensuing discussion:

$\underline{i}$ is the intensity of radiant energy which strikes the photographic plate. Strictly speaking, the plate does not measure intensity (energy per unit time) but rather integrated intensity or total energy.³⁰ In most analytical work, however, since an internal standard is employed to correct for variations in the exposure conditions, all energies are stated in terms of relative intensities of analysis line to internal standard lines. Here, it makes no difference whether the effect is stated as energy per unit time or as total energy. The absolute value of $\underline{i}$ is never determined in analytical work. All intensity values are stated in relative terms based upon the empirical scale given by a plate calibration curve. $\underline{I}$ and $\underline{I}_0$ refer to the intensity of light transmitted by a developed photographic plate, as measured by a microphotometer. The symbol $\underline{I}$ is the photometer reading for the light transmitted by an exposed portion of the plate, usually a spectrum line; $\underline{I}_0$ is the photometer reading for a clear unexposed portion of the same plate. In all measurements, the ratio of the two readings is needed to express the photographic effect. The ratio is expressed in various ways as transmission, opacity, or density.

²⁹A. Hay, "Handbuch der Wissenschaftliche und Angewandten Photographie," Springer, Wien, 1930, Bd. IV.

³⁰M. Slavin, Ind. Eng. Chem. Anal. Ed., 10, 407 (1938).

Transmission, $\underline{T}$, is defined by the expression

$$\underline{T} = \frac{\underline{I}}{\underline{I}_0} . \quad \text{Eq. 1}$$

Opacity, $\underline{O}$, is the reciprocal of transmission. Density, $\underline{D}$, is defined by the relation

$$\underline{D} = \log_{10} \frac{\underline{I}_0}{\underline{I}} = \log_{10} \text{ Opacity.} \quad \text{Eq. 2}$$

Density is a more fundamental concept for expressing photographic response than opacity, because density is a linear function of visual response.³¹ Moreover, density is proportional to the mass of developed silver in the emulsion.³² The relation between density and light intensity is usually expressed by an H & D curve,³³ which is a plot of density against log relative intensity or log relative exposure time. Examples of such H & D curves are shown in Figures 12 and 18. The reason for plotting plate response in this way is the fact that the curve so obtained has a long linear portion which, for some plates, may extend from a density of 0.30 to above 2.0. Further, this type of graph is convenient for obtaining the intensity ratio of two lines, for the difference along the log relative exposure axis is the logarithm of the intensity ratio desired. Another useful type of plate response curve is shown in Figure 11; here density is plotted against intensity or exposure time. The advantage of this method is that any density value can readily be converted into an arbitrary intensity value. A disadvantage is that the curve has no linear portion.

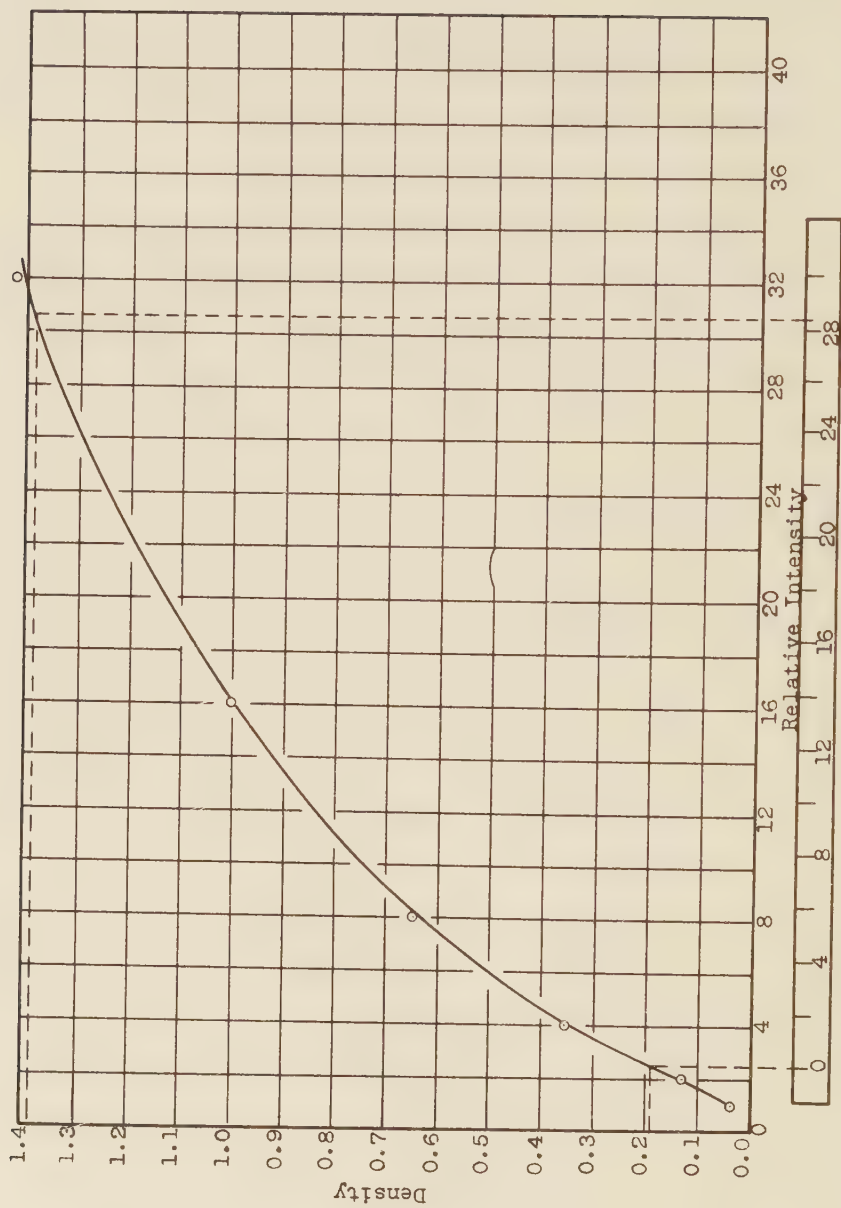
Plate Calibration

Photographic intensity measurements are made by comparing the density of the line to be measured with the density of a line of known relative intensity. Since the effect produced by a given number of light quanta depends upon the properties of the plate, the wave length of the light, the developer used, the temperature and time of development, and certain other second-order factors,

³¹F. E. Ross, J. Opt. Soc. Am., 4, 255 (1920).

³²Ibid.

³³F. Hurter and V. C. Driffield, Jour. Soc. Chem. Ind., 9, 455 (1890).



Sliding Scale for Subtraction of Background Intensity
 Fig. 11.--Plate calibration curve (density against intensity)

it is necessary to calibrate each plate or else to regulate the above factors so closely that a single H & D curve will suffice for a given lot of plates. Such a curve is constructed by placing on the plate a series of exposures of known relative intensity, measuring the densities of the resulting images, and plotting these densities against some function of the corresponding intensities.

The comparison of intensities by means of the photographic effects produced is subject to several kinds of error.³⁴ Strictly speaking, such a comparison is accurate only when:

1. The exposures are made simultaneously and non-intermittently.
2. The wave lengths of the compared radiations are equal.
3. The comparison is between lines of equal density.
4. The comparison is between lines lying on adjacent portions of the emulsion.

It is not possible to fulfill these conditions in routine analytical work. The plate calibration exposures are often intermittent and cannot be made simultaneously with the analysis exposures. Lines to be compared with one another are often widely separated on the plate. Often it is necessary to make comparisons between lines of widely different densities. It is necessary, therefore, to determine to what extent the departure from ideal conditions affects the accuracy of intensity measurements. The first point to be investigated is the method for making exposures of known relative intensity to be used in the construction of calibration curves. There are three general methods for making such exposures:

(1) Stepped Sector.--A rotating sector with stepped openings of known relative values is placed before the slit, which is uniformly illuminated from top to bottom. The spectrum obtained consists of steps of known relative exposure time. A source giving either continuous light or lines may be used for illumination.

(2) Stepped Weakener.--A neutral wedge, made by sputtering a quartz plate with reflecting or absorbing material (such as platinum or aluminum) in steps of known relative transmission, is placed before the slit. Either continuous or monochromatic radia-

³⁴L. Jones, "Measurement of Radiant Energy," ed. by Forsythe, McGraw-Hill, 1937, chap. viii, p. 246.

tion may be used; the resulting spectrum consists of steps for which the relative intensities are known.

(3) Stepped Slit.--The spectrograph slit is opened wide and is replaced by a slit with a series of stepped openings of known widths. A source of continuous radiation must be used for illumination, in order that the number of light quanta striking unit area of the plate be proportional to the width of the slit in each step.

Each of these methods has advantages and disadvantages. The stepped sector is easiest to construct and use; moreover, it gives the same relative transmission in the various steps, regardless of the wave length. It has long been mistrusted, however, because it gives intermittent exposures and because it may cause possible reciprocity failures due to the unequal time of illumination for the several steps. The stepped weakener is theoretically the most reliable device, but it is a research job to prepare and calibrate the absorbing layers and to insure that the relative transmission of the steps is the same for all wave lengths.³⁵ The stepped slit is difficult to make accurately, since the width of the smallest opening must be ≤ 0.125 mm. if five steps which have a transmission ratio of two to one are to be obtained. A further disadvantage of this instrument is the difficulty of obtaining a suitable source of continuous radiation in the ultraviolet region commonly employed for spectrochemical analysis. This source must have a fairly uniform intensity distribution over the whole wave length region of interest, since the spectral purity of the image is a function of the slit width in the various steps; in a region of abrupt intensity change, the image given by the widest step will be formed by more overlapping wave-lengths than the image given by the narrowest step.

Recently, the step sector method has grown in favor, since Webb³⁶ has shown that reciprocity failures disappear when illumination is made by intermittent exposures of high interruption frequency. His results are summarized in the statement:

If the frequency of interruption is sufficiently high, an intermittent time-scale exposure becomes identical with an intensity-scale exposure. The critical frequency is a rate

³⁵E. von Angerer, "Wissenschaftliche Photographie," Akademische Verlagsgesellschaft, Leipzig, 1931, p. 145.

³⁶Webb. J. Opt. Soc. Am., 23, 157 (1933).

of interruption sufficiently high that each individual silver halide grain receives on the average approximately one quantum per flash.

Experiments were performed to test whether, under the conditions employed in analysis, this equivalence between intermittent and uninterrupted light really exists. In these experiments, a comparison was made between plate calibrations obtained by use of the stepped slit and those obtained by the stepped sector.

A five step slit was constructed to fit in the wedge guides of the spectrograph. Each step was 2 mm. in height; the widths of the steps were made approximately 0.125, 0.25, 0.50, 1.0, and 2.0 mm. The exact widths were determined at various positions by measurement with a filar micrometer, and an average was taken for each step. Illumination was from an underwater spark between tungsten electrodes energized by a Tesla coil. This source gave continuous radiation extending down to a wave length near 2500Å, with a fairly uniform distribution of intensity over the range 2500-3400 Å used in this study. A Hilger Littrow spectrograph was employed. The source was placed about two meters from the slit with no intervening lens, so that uniform illumination was obtained from top to bottom. Exposure times of five to eight minutes gave spectra of densities suitable for measurement. The process plates used were developed by rocking for two minutes at 18°C. in Eastman D9 developer. The densities of the various steps were measured at a wave length of 3000 Å. H & D curves were constructed by plotting densities against $\log_2$ relative exposures. This log scale was chosen because the slits were made so that the $\log_2$ values for the relative slit widths were 0, 1, 2, 3, and 4.

A seven step rotating sector was constructed from a brass disc. The largest angular opening was 180°; each succeeding opening was half as large as the preceding one. Each step was 2 mm. in height. The sector was mounted on the shaft of a small motor whose speed was 1800 r.p.m. and the whole assembly so placed on the optical bench that the sector stood 1 cm. from the slit. Exposures were made with the continuous source described above and also with a mercury vacuum vapor lamp operated on a 220 volt d.c. source. H & D plots of density against $\log_2$ relative exposure were made (as in the stepped slit experiments) at 3000 Å for the continuous source and at 2967 Å for the spectrum made from the

mercury vapor arc.

The three H & D curves obtained respectively, for the stepped slit, the stepped sector with continuous radiation, and the stepped sector with monochromatic radiation, were found to be equivalent within experimental error; all three had the same slope in the linear portion and were very nearly parallel to one another in the toe portion (Figure 12). In further experiments where the mercury vapor lamp was used as a source, interruption frequencies as low as 100 per minute were found to give curves identical with those obtained at higher frequencies (1800 r.p.m.). This result is in agreement with those of Malpica,³⁷ who reports no difference in plate gamma for sector speeds varying from 1 to 3600 interruptions per minute.

From the results of these experiments, it appears that the stepped sector may be trusted as a calibration source; it seems to introduce no errors due to reciprocity failure or intermittency effect over the range of wave length and intensity studied. Since it is easy to construct and to use the sector, this method is recommended for plate calibration. The following conditions have been found to give good results. A suitable source of line radiation is mounted 1.5 to 3 meters from the slit so that uniform illumination is assured. No lenses are used between the source and the slit. The source is operated at such intensity that an exposure of three to six minutes gives lines of density suitable for measurement. The sector is mounted on the shaft of a small induction motor and left permanently in position just before the slit; during the calibration exposure it is rotated, but is left in the open position during the analysis exposures. The source is mounted on a pivoted arm so that it can be moved back and forth during the exposure to permit the beam of light to traverse the collimator lens of the spectrograph. With the source in a fixed position, only a narrow area of the lens and prism is utilized and the lines obtained are not flat. (A fixed source might be used if a long focus lens were placed just before the slit, to diffuse the light over the whole collimator lens.) It is convenient to mount the calibration source on a position at right angles to the optical path, so that no equipment need be removed from the optical bench before making a calibration expo-

³⁷M. Malpica, Gen. Elec. Rev., 43, No. 7, 288 (1940).

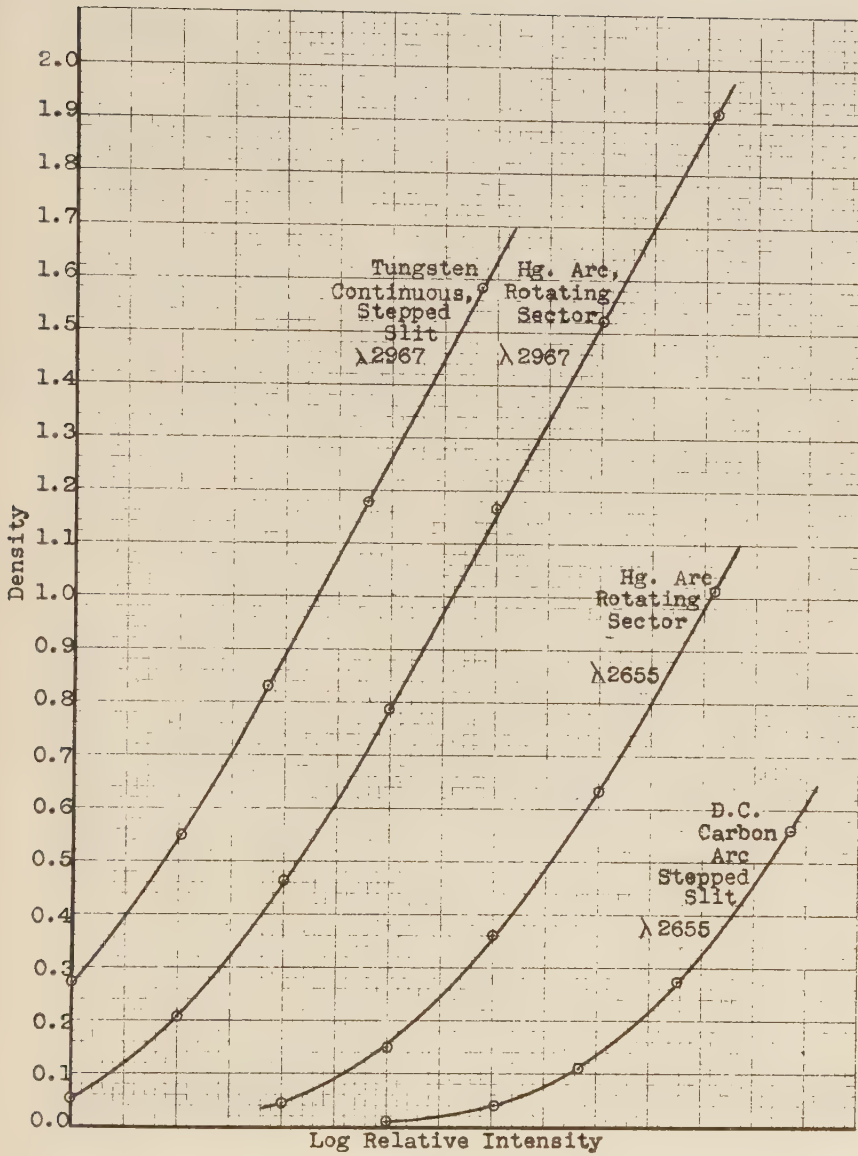


Fig. 12.--H & D Curves for continuous and monochromatic light

sure. This source may be permanently fixed in position and the light brought onto the slit by means of a right angle quartz prism set before the slit for calibration exposures.

The source must give well-separated lines in the desired analytical region and must give a spectrum which is entirely free from background adjacent to the lines. A vacuum mercury vapor lamp operated on direct current was first used in this work with excellent results. Later it was found that equally good results could be obtained from a 5-amp. arc between brass electrodes. Massive electrodes (diameter 15-20 mm.) must be used to avoid heating the anode to incandescence.

It has been found, from the results of many plates, that calibration of every plate is unnecessary; in general, it is sufficient to calibrate one plate from a box of twelve, provided that a standardized procedure is used for development. Exact control of both the temperature and the agitation of the developer are important. Good results have been obtained by rapid rocking or by brushing of the plate during development. In the latter method, the tray is left motionless and the emulsion is brushed by long sweeps of a camel's hair brush, so that each part of the emulsion received approximately the same number of strokes.

It is not necessary to use a seven step sector, like the one described above. For most purposes it is sufficient to use a sector with four steps, provided that an uninterrupted portion of the beam is allowed to pass above the sector to make a fifth step. The exposure should be so timed that the desired line has a density of 0.04-0.06 in the lowest exposure step. The density of the highest exposure step will then fall on the linear portion of the H & D curve, which can be extrapolated by prolonging the linear portion up to a density of 2 or more. The validity of the extrapolation can at any time be confirmed by constructing a curve for a stronger line of the same spectrum and plotting these data on the same scale, so as to extend the curve to higher densities.

It has long been known that photographic plates are subject to a type of error called "reciprocity failure"; that is, if a photographic plate be exposed to two radiations of intensity i_1 and i_2 for such times that

$$i_1 t_1 = i_2 t_2 \quad \text{Eq. 3}$$

the densities of the two images will not, in general, be equal. Differently stated, there is an optimum intensity such that, for

the production of an image of given density, the product $i \times t$ is a minimum. Among the attempts to find the correct relation between intensity and time for the production of images of a given density is the celebrated equation of Schwarzschild:³⁸

$$i_1 t_1^p = i_2 t_2^p \quad \text{Eq. 4}$$

in which the parameter p has a value near 0.9, depending upon the emulsion characteristics and the intensity range. Another way of expressing the Schwarzschild Law is:

$$D = f(i \cdot t^p) \quad \text{Eq. 4}$$

Suppose that two portions of a plate be exposed respectively to two different radiations of intensity i_1 and i_2 for a given time, t_1 , and that the densities of the resulting images are D_1 and D_2 . Suppose also, that two other portions of the plate are exposed respectively to light of intensity i_1 for times t_1 and t_2 , such that the resulting images have the same respective densities, D_1 and D_2 . Then the two images of density D_1 are the results of two exposures of the same time and intensity. The two images of density D_2 result from exposures $i_2 t_1$ and $i_1 t_2$.

The Bunsen-Roscoe Law would require that $i_1 t_2 = i_2 t_1$ for images of equal density.³⁹ The Schwarzschild Law states that the two images will be of equal density if the expression

$$i_1 t_2^p = i_2 t_1^p \quad \text{Eq. 5}$$

is fulfilled.

The condition of equal density has already been imposed, and the values of i_1, i_2, t_1 , and t_2 specified. The parameter, p , is thus determined.

Since

$$\frac{i_1}{i_2} = \left(\frac{t_1}{t_2} \right)^p$$

$$p = \frac{\log \frac{i_1}{i_2}}{\log \frac{t_1}{t_2}} \quad \text{Eq. 6}$$

Hypothetical D against $\log i$ and D against $\log t$ curves are

³⁸K. Schwarzschild, Astrophys. Jour., 11, 89 (1900).

³⁹Bunsen and Roscoe, Pogg. Ann., 96, 96; 100, 43; 101, 255; 108, 193 (1876).

shown in Figure 13. The equations of the straight line portions of the two curves are:

$$D_1 - D_2 = \gamma_i \log \frac{i_1}{i_2}, \text{ and} \quad \text{Eq. 7}$$

$$D_1 - D_2 = \gamma_t \log \frac{t_1}{t_2}, \quad \text{Eq. 8}$$

where γ_i and γ_t are respectively the slopes of the D against $\log i$ and D against $\log t$ curves.

From equations 6, 7, and 8:

$$p = \frac{\gamma_t}{\gamma_i}. \quad \text{Eq. 9}$$

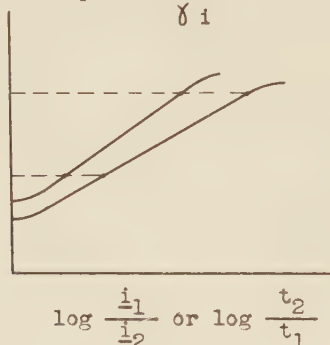


Fig. 13.-- D against $\log i$ and D against $\log t$ curves

If $p < 1$, the density against log time curve should be flatter than the density against log intensity curve. Experimentally, the gammas of the two curves are identical for the light intensities and exposure times encountered in spectrochemical analysis, indicating no reciprocity failure due to plate calibration by means of a rotating sector.

The perfect agreement obtained for calibration curves made by continuous and by monochromatic light contradicts the results of Strock,⁴⁰ who finds that the plate gamma is much steeper for a spectrum line than for continuous radiation. His experiments were made with light of the visible region, and presumably

⁴⁰L. W. Strock, "Spectrum Analysis with the Carbon Arc Cathode Layer," Hilger, London, 1936, p. 32.

with sensitized plates; the difference may be due to an Eberhard effect in the development. Because of his work, similar discrepancies have been generally assumed for all wave lengths and for all plates. Consequently, it has been assumed that in all regions, the effect of background is different from the effect produced by monochromatic light of the same frequency. This assumption has retarded the successful application of background corrections which, as will be shown later, are often essential for accurate work. The results reported in this dissertation show that non-sensitized plates give, in the ultraviolet region, the same response per quantum of light of given wave length, regardless of whether the light be continuous or monochromatic. It appears that the discrepancy may be due to the differences in wave length, in the emulsion characteristics of the plates, and above all, to the differences in development technique. In this connection it must be mentioned that the conclusions of the present work are based altogether upon work with unsensitized plates in the region 2500-3400 Å; none of the conclusions reached can safely be assumed to be valid for work in the visible region.

Variation of Gamma with Wave Length

It is well recognized that plate gamma is a function of wave length, but unfortunately, most of the data published about this effect are for wave lengths above 3500 Å. Consequently, it was necessary to investigate the magnitude of the effect in the analytical region 2500-3400 Å for Eastman Process and Spectrum Analysis No. 1 plates. Results for Process Plates are shown in Figure 14. H & D curves are strictly parallel to one another throughout the region 2500-3100 Å, but above 3100 Å the slope of the curves increases with increasing wave length. Similar results were found for Spectrum Analysis No. 1 plates, except that the gamma value is greater in all regions than it is for Process plates.

Since the plate gamma is constant for the region 2500-3100 Å, a single calibration curve suffices for all lines in this region, and a single internal standard line may be used for all lines. At higher wave lengths, the plate must be calibrated for the wave length region containing the analysis and the internal standard lines which must lie close together.

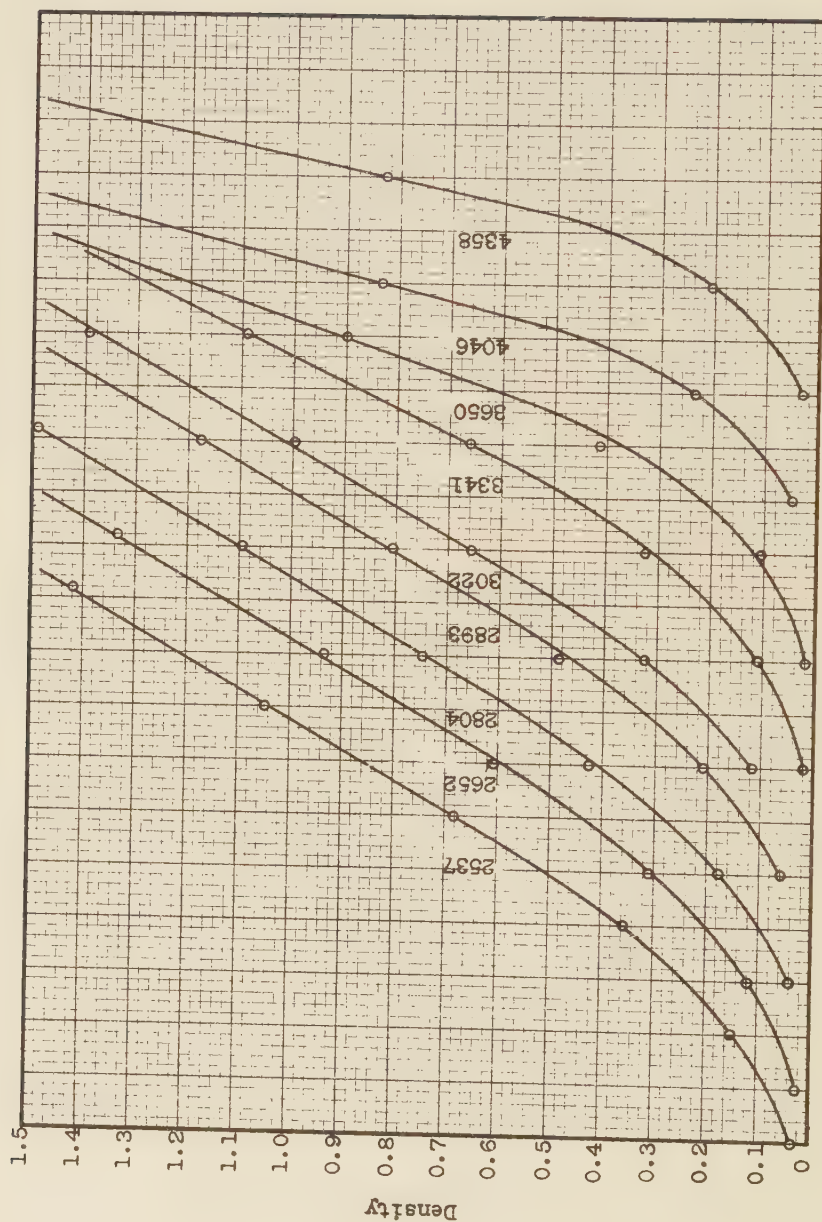


Fig. 14.--Variation of Plate Gamma with wave length

Accuracy of Intensity Measurements

The accuracy of spectrochemical analysis is influenced by two types of errors, (a) unequal vaporization and excitation of the constituents of the sample, and (b) errors in the photographic process. In order to investigate the latter errors independently of any errors in excitation, relative intensity ratios were determined for several steps of a line pair in a single spectrum, which was photographed by means of the stepped sector used for calibration. Since the actual intensity ratio for a given line pair is the same for all steps, any variations found should be attributed to errors in the photometric procedure.

The spectrum of a mercury vapor lamp was recorded by means of a seven step sector, in the manner described for plate calibration. A plate calibration curve was constructed for the 2894 Å line. By means of this calibration curve, relative intensity values were determined for all measureable steps of the 2652, 2654, and 2655 Å lines; intensity ratios were then computed for corresponding steps. These ratios for the various line pairs are given in Table 1. In further tests, intensity ratios were determined for the same line pairs taken from several spectra photographed on different plates. The results are summarized in Table 2.

TABLE 1

INTENSITY RATIOS OF LINE PAIRS IN A SINGLE STEPPED SPECTRUM

Step	Intensity $\frac{2652}{2654}$	Intensity $\frac{2652}{2655}$	Intensity $\frac{2654}{2655}$
1	2.14	3.47	1.62
2	2.07	3.35	1.62
3	1.97	3.26	1.66
4	2.10	3.36	1.65
5	2.14		
6			
Average	2.08	3.36	1.64
Average dev'n in %	2.4	1.6	1.05

No attempt was made to obtain the highest precision by averaging the results of several photometer readings for the same line or to separate the errors in measurement from those inherent in the photographic process. The object was rather to maintain the conditions of a routine analysis, so that the results would be applicable to ordinary work. A wide intensity range, from about 0.1 to 1.6 density units was included. Under these conditions the average deviations were about 2-3 per cent, with occasional deviations of as much as 5-7 per cent.

In addition to the above errors, which are due to failures in the photographic plate and in the developing technique, there are certain errors which arise in the photometry of the lines. These last depend upon the nature of the response of the emulsion to light and upon the fact that the accuracy of deflection-type densitometric measurements varies with the density of the image. If i be the intensity of the light producing the line, and I be the galvanometer deflection produced by the light transmitted by the line, the error involved in the estimation of the intensity of the source light is:

$$E = \frac{1}{I} \cdot \frac{d i}{d I} \quad \text{Eq. 10}$$

Since $d \log i = d i/i$, the slope of the curve obtained by plotting $\log i$ against I gives the relative error for any value of i . The minimum in the curve obtained by plotting $(d \log i) / d I$ against I gives the galvanometer deflection to which the greatest accuracy of intensity measurement corresponds. The optimum line density for photometry is then $\log \frac{I_0}{I^*}$, where, as before, I^* is the galvanometer deflection associated with the minimum in the second derivative curve. Figure 15 shows the error curve superimposed upon the $\log i$ against I curve. The density to which the most accurate estimate of intensity corresponds is 0.25. Densities either larger or smaller than this optimum entail larger errors in the determination of light intensity. For example, the errors are twice as large for densities of 0.066 and 0.724 as compared with 0.25, and seven times as large for a density of 1.30. The spectroscopist should, therefore, limit line densities to the range 0.03 to 0.90, in so far as it is possible to do so.

.The precision actually obtainable in the analysis of homog-

TABLE 2
INTENSITY RATIOS OF LINE PAIRS FROM STEPPED SPECTRA
OF SEVERAL PLATES

Intensity $\frac{2652}{2654}$	Intensity $\frac{2652}{2655}$	Intensity $\frac{2654}{2655}$
2.14	3.47	1.62
2.07	3.35	1.62
1.97	3.26	1.66
2.10	3.36	1.65
2.14	3.54	1.65
2.14	3.32	1.57
2.14	3.40	1.61
2.14	3.27	1.57
2.10	3.46	1.60
2.10	3.32	1.61
2.07	3.40	1.61
2.13	3.37	1.61
2.09	3.49	1.59
2.19	3.22	1.59
2.04	3.25	1.62
2.03	3.03	1.49
2.07	3.24	1.63
2.00	3.24	1.62
2.00	3.36	1.62
1.93	3.36	1.65
2.14	3.47	1.65
2.05	3.36	1.66
2.08	3.42	1.66
2.14	3.24	1.56
Average dev'n in % 2.4	2.7	1.8

enous metal samples is comparable to that of the experiments on photographic plate errors. This statement is confirmed by the data of Table 3, which were obtained by Tlapa⁴¹ in the determination of silver and bismuth in lead samples; his excitation source was a high voltage spark with a synchronous interrupter. Results of about the same precision are given by Sawyer and Vincent⁴² for the determination of minor constituents in steel by the use of an alternating current source. From these examples the limiting fac-

⁴¹C. J. Tlapa, op. cit.

⁴²R. Sawyer and H. Vincent, J. Appl. Phys., 8, 163 (1937).

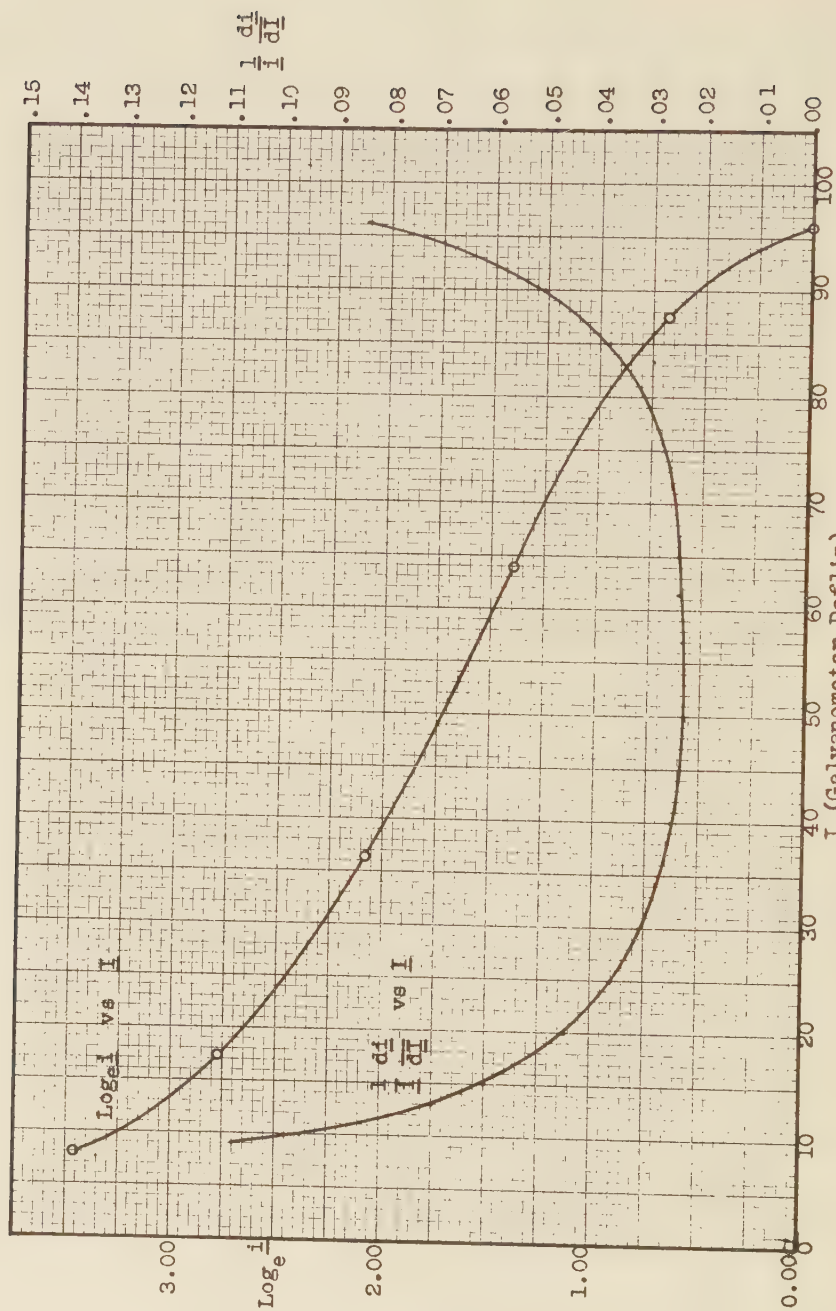


Fig. 15.--Optimum photometerable density

tor in the accuracy of spectrochemical analysis appears to be the photometric process with its attendant plate errors, provided that favorable excitation conditions are employed. The accuracy is not nearly so good, however, for those analyses in which a carbon supporting electrode must be used. In such analyses, a mean deviation of ± 5 per cent in a series of duplicate determinations is good; quite often it is not possible to obtain a precision better than 10 per cent. Here, the limiting factor appears to be unequal vaporization and excitation of the constituents of the sample; only a small portion of the error should be attributed to errors in the photographic process.

TABLE 3
PRECISION OBTAINABLE IN SPARK ANALYSES

Per Cent Ag	Deviation	Per Cent Bi	Deviation
0.0056	0.0001	0.0315	0.0002
57	2	315	2
54	1	310	7
55	0	315	2
51	4	(280)	-
55	0	315	2
55	0	310	7
55	0	335	18
55	0	315	2
56	1	310	7
55	0	315	2
57	2	335	18
Average 0.0055	.000092	0.0317	0.0006

Average deviation for Ag = 1.67%; for Bi = 1.9%
Maximum deviation for Ag = 7.3%; for Bi = 5.7%

The Effect of Background

When a spectrum line lies in a region of heavy background, the density value obtained for it is high, and a correction must be applied for the density contributed by the background. This correction cannot be obtained by subtracting the background density from the total density or by the equivalent procedure of making the I_0 reading in the background region. Rather, it is neces-

sary to subtract the background intensity from the total intensity. The method of making this correction is shown in Figure 11 by dotted lines. The total density of 1.37 corresponds to a relative intensity of 30.9 (arbitrary units). The background density of 0.19 corresponds to a relative intensity of 2.4. Subtraction gives a corrected line intensity of 28.5. If, for the same values, an attempt is made to correct by subtraction of densities, a "corrected" line intensity of 22 is obtained, which is too low by about 25 per cent. The validity of the above method for making background corrections was tested in the following experiment next described.

Two seven step mercury arc spectra were photographed on a plate. On one of the spectra a heavy background was superimposed by re-exposing that portion of the plate to the spectrum from a carbon arc. Intensity ratios were determined for the various steps of the 2652 and 2654 Å lines in the spectrum without background, in the spectrum with background, and in the spectrum with background corrected as described above. The results are shown in Table 4. After correction, the intensity ratios for the various steps are reasonably good; but that if the uncorrected ratios are used, the values for the lowest exposure steps are in error by as much as 40-50 per cent. Data for the same plate are shown in the H & D curves of Figure 16. Curve A is for the spectrum without background, curve B for the one with background. It will be noted that at high intensities, the effect of background is not great, but that in the lower exposure steps the measured density is chiefly that of the background. Curve C showing the corrected line densities is in good agreement with Curve A.

TABLE 4
BACKGROUND INTENSITY CORRECTIONS

Step	Intensity Ratio Without Background	Intensity Ratio With Background	Intensity Ratio Corrected for Background
1	2.14	1.85	2.00
2	2.07	1.84	1.86
3	2.06	1.61	1.98
4	2.08	1.40	1.87
5	2.03	1.22	1.83
6		1.12	1.94

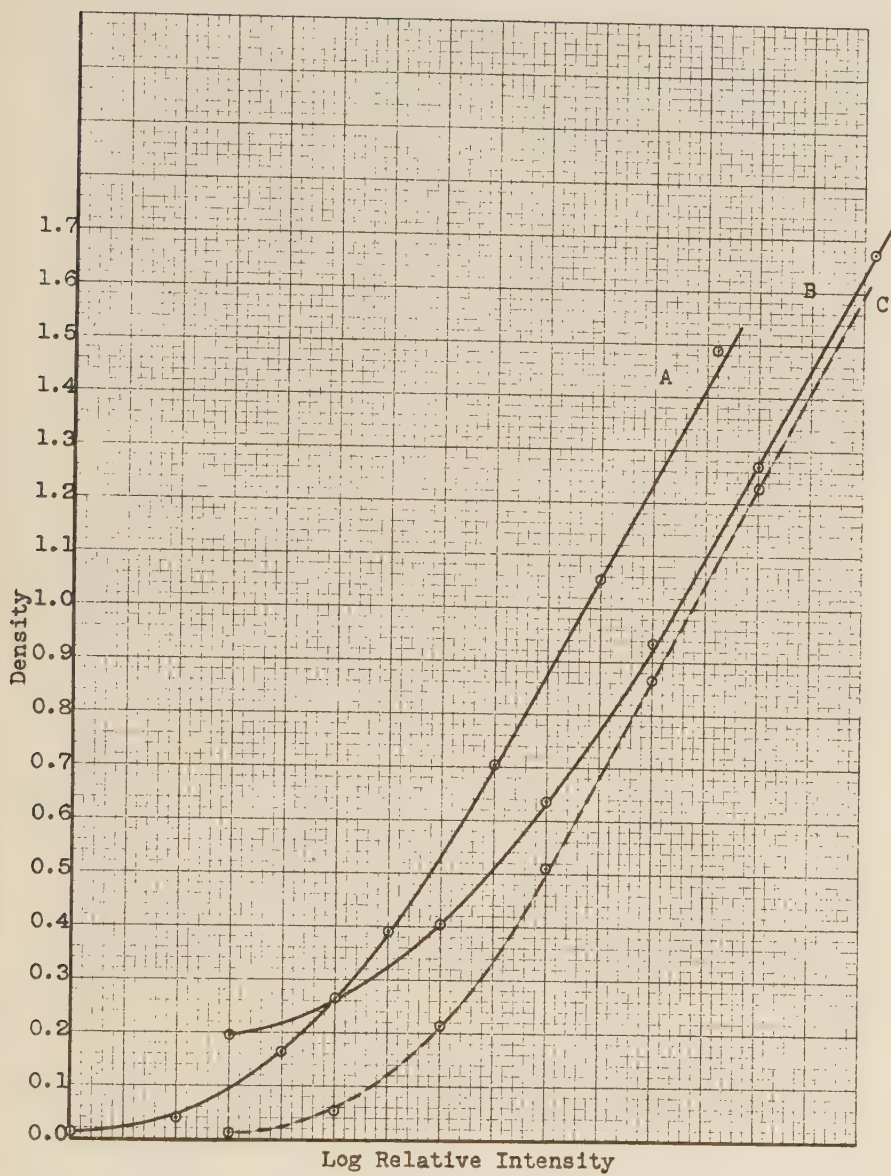


Fig. 16.--Background effect

The effect of background in analytical work is shown in the working curves of Figure 17. The heavy line shows the working curve for the Al:3082 Å line, made with the alternating current arc. The sample was a 3.6 molar solution of sodium hydroxide to which known amounts of aluminum had been added. All concentrations are based on the weight of dry NaOH. Mo: 2816 Å was used as the internal standard line. The circles give the intensity ratios corrected for background and for the residual amount of aluminum in the NaOH. The dotted curve gives the intensity ratios obtained where no background correction is applied. At high concentrations the two curves are nearly parallel to one another, but at low concentrations the uncorrected values indicate concentrations which are several hundred per cent in error. In fact, the curvature of the uncorrected line is like that obtained when the matrix holds a considerable residuum of the element sought. Were the background correction not applied, one might over-correct for the residuum present.

It follows from the results just presented that the plate calibration curve must be made from a background-free spectrum, for unless the true calibration curve is known down to low density values, accurate background corrections cannot be made. It is, therefore, not a good practice to make the calibration curve from a stepped exposure with analysis samples, because spectra thus produced usually contain a rather heavy background, especially if a carbon supporting electrode is employed. Some workers use no separate plate calibration curve, but make all exposures with a stepped sector, and plot H & D curves for every line. The concentration is then determined from the linear separation on the log exposure axis of the internal standard and analysis lines. This practice, although it partially eliminates the effect of background, leads to some error for faint lines because the density measured here is largely that of the background. (See curve B of Figure 16.)

Treatment of Experimental Data

The microphotometer data obtained from spectra are in the form of galvanometer deflections for clear plate and for spectral lines, as a rule. From these readings, intensity ratios for internal standard and analysis lines are obtained. The working curve may be any type of graph which relates a function of the

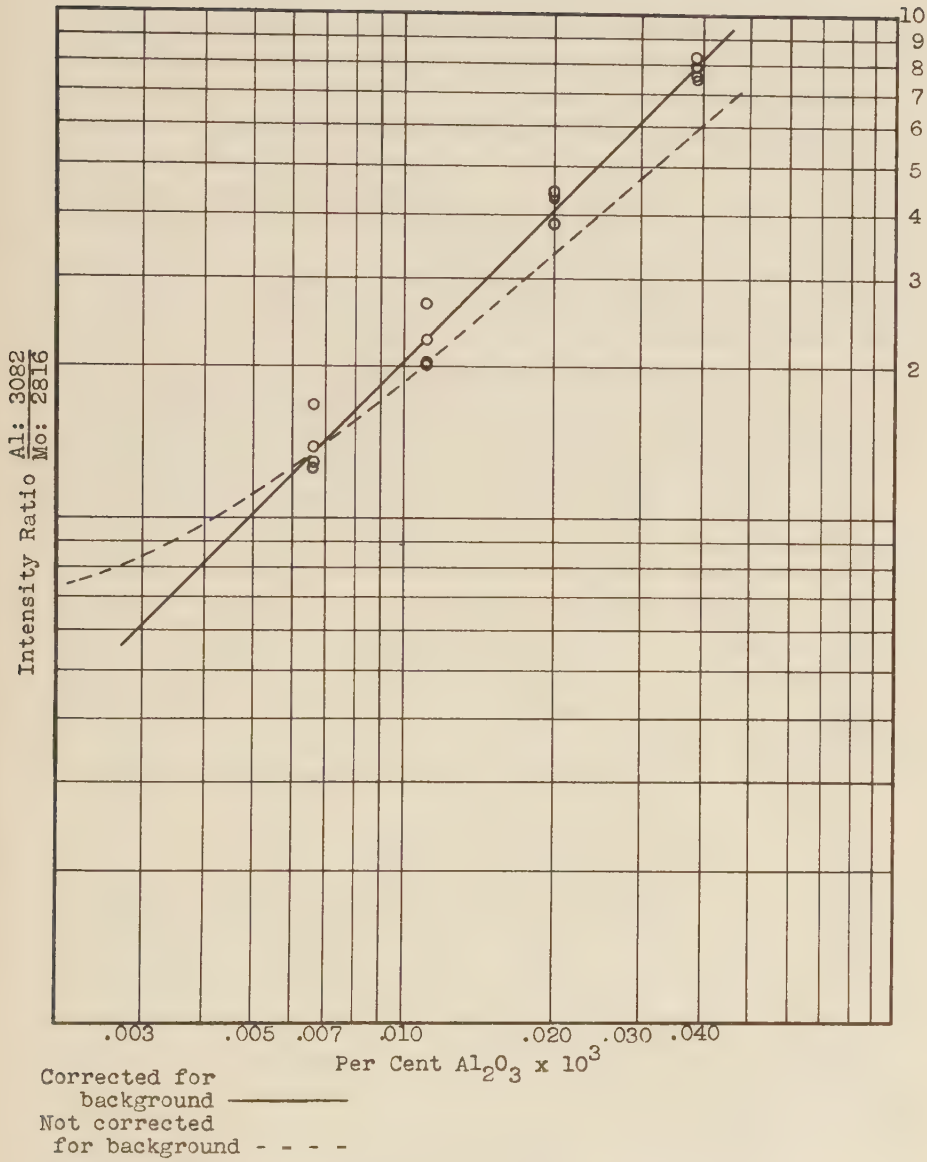


Fig. 17.--Effect of background correction on working curve

galvanometer readings to a function of the concentration. The labor of computation may, however, be materially lightened by the proper choice of these functions.

It is generally advantageous to plot the plate calibration curve on a density-log relative intensity basis, when background corrections are not needed, because the curve so obtained has a long linear portion. It is not necessary, however, actually to convert galvanometer readings into densities. If the photometer light intensity is so adjusted that the reading for the clear plate is 100, the readings for the lines are the percentage transmission values. These may be plotted against relative intensities by use of log-log paper (see Figure 18). When background corrections are needed, however, it is advantageous to plot density against intensity. Here semi-log paper can be used, with galvanometer readings on the log scale (Figure 18) but with intensity values on a linear scale (Figure 11).

Calculating boards of the type described by Owens⁴³ are advantageously used with either type of graph. The method for using the board to obtain intensity ratios when background corrections are not necessary is shown by the dotted lines in Figure 18. The sliding scale at the bottom, graduated to agree with the x-axis, gives the intensity ratio of two lines of the densities indicated. When background corrections are necessary, intensity ratios cannot be obtained directly by a single graphical operation. Instead, the board is used to make the background corrections (as indicated by the dotted lines of Figure 11), and the ratios of the corrected intensities of internal standard and analysis lines are determined by a separate slide rule operation.

Working Curves

Every spectrographic analysis is based upon a comparison of the intensity values obtained from an analysis sample with the values obtained from samples of known composition. The working curve, which relates a function of intensity to a function of concentration, has in the past been expressed in many different ways; recently the practice has become quite standardized, since today nearly everyone uses an internal standard whenever possible.

⁴³J. S. Owens, "Proc. Fifth Summer Conf. on Spectroscopy and Its Applications," John Wiley & Sons, New York, 1938, p. 17.

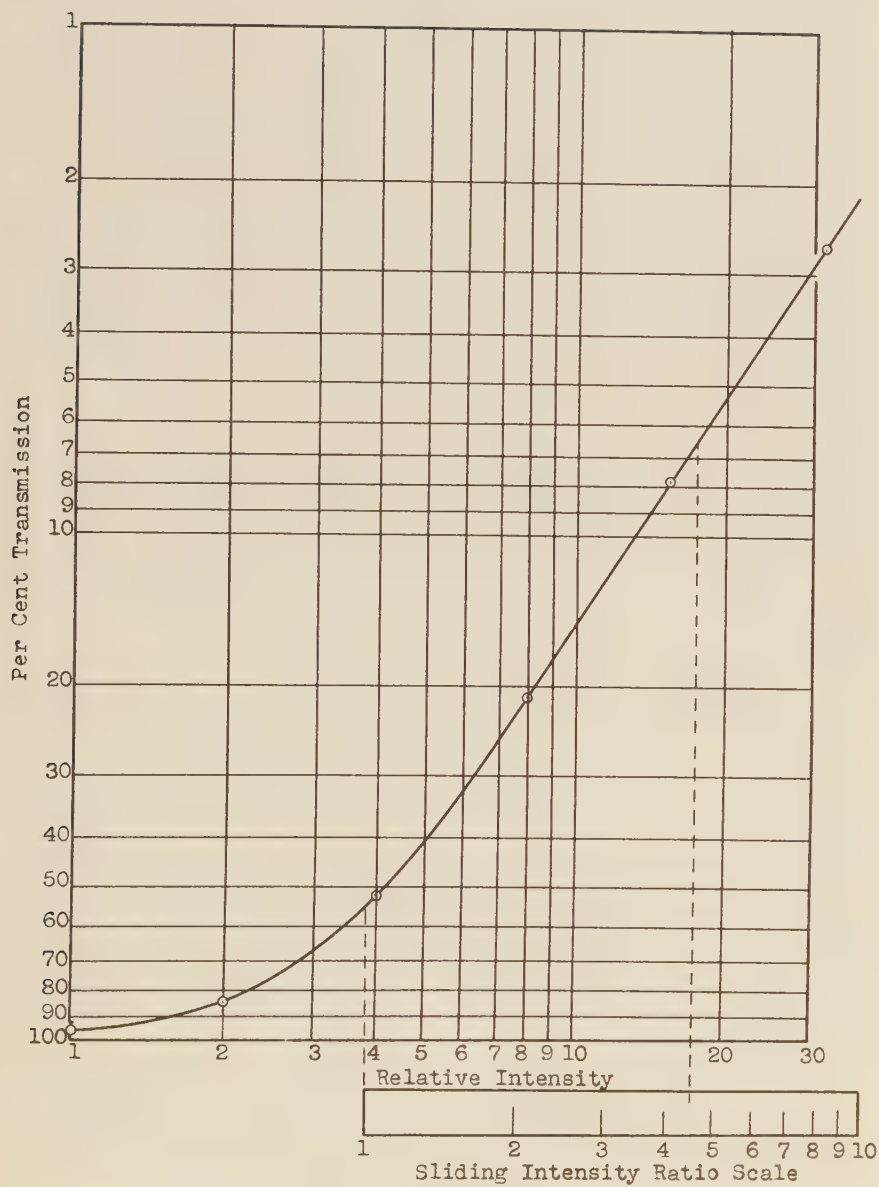


Fig. 18.--H & D curve on log-log paper

The relation between the intensity of light emitted within a source and the concentration of the emitting atoms is linear. That is,

$$\underline{i} = kC \quad \text{Eq. 11}$$

or, if an internal standard is used,

$$\underline{i}_A / \underline{i}_S = kC_A \quad \text{Eq. 12}$$

where $\underline{i}_A$ and $\underline{i}_S$ are respectively the intensities of analysis and internal standard lines, and C_A is the concentration of the constituent to be determined.

Unfortunately, the intensity of light emitted from a source is not always a linear function of the concentration; some of the emitted light is often re-absorbed in colder outer layers of the source. When such absorption occurs, the relation between concentration and intensity is given by an empirical equation of the form

$$\underline{i}_A / \underline{i}_S = kC_A^{\underline{n}} \quad \text{Eq. 13}$$

where $\underline{n}$ is a number less than unity. The mechanism of light absorption is doubtless complicated, since the light traverses outer gaseous layers of varying temperatures before it can be detected; a simple Beer's Law absorption does not lead to the empirical intensity-concentration equation given above. Consequently, this relation cannot be assumed to hold in all cases, although no evidence to the contrary has been found.

Regardless of whether self-absorption occurs or not, a plot of log intensity ratio against log concentration gives a straight line of slope $\underline{n}$. The value of $\underline{n}$ is unity when there is no absorption--less than unity when absorption occurs. Thus, when there is no absorption, either intensity ratio against concentration or log intensity ratio against log concentration may be plotted; a straight line is obtained by either method. The Al:3082 and Si; 2816 Å lines are examples of non-absorbed lines. When there is absorption, only the log intensity- log concentration plot gives a straight line; consequently, this form of plot is generally used.

The value of $\underline{n}$ varies, as one might expect, with different lines of the same element. An example of this phenomenon is shown in Figure 19, which gives Tlapa's⁴⁴ results for the two sil-

⁴⁴C. J. Tlapa, op. cit.

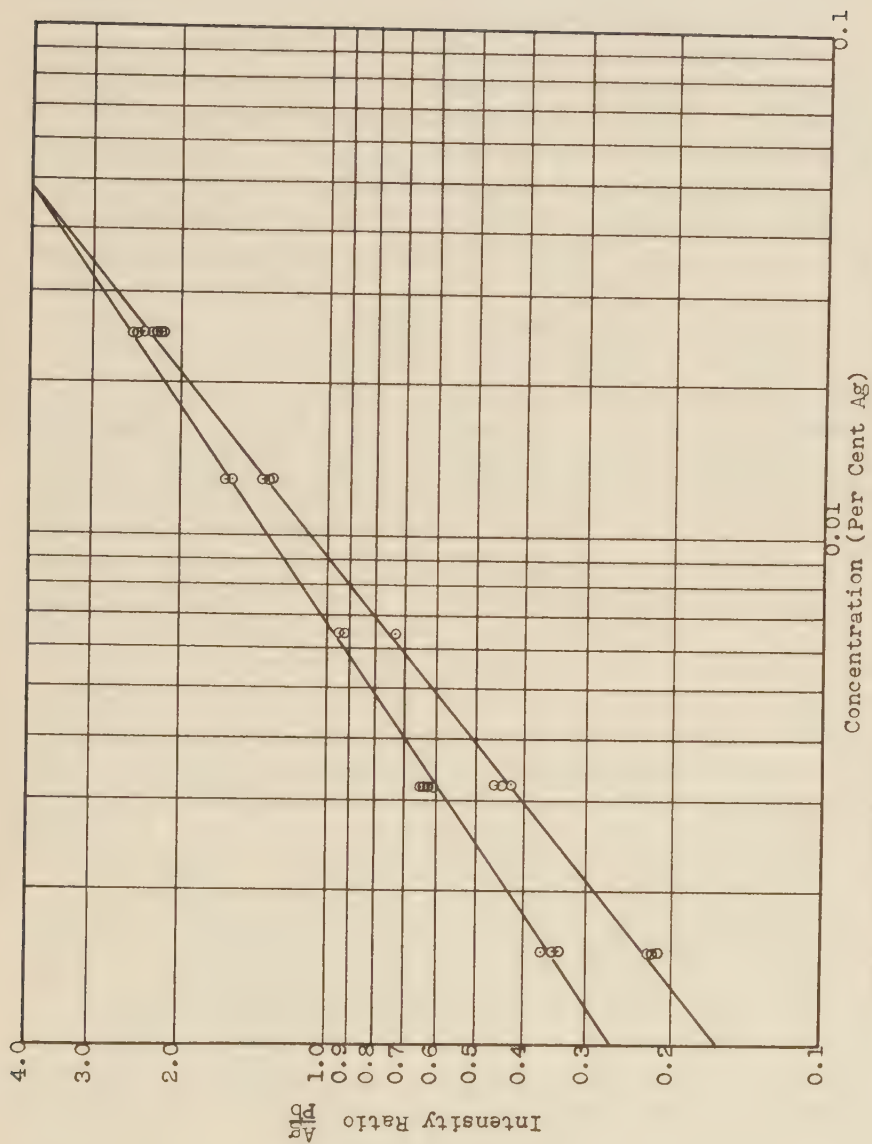


Fig. 19.--Variation in slope of working curves of silver in lead

ver lines 3281 and 3381 Å. At low concentrations, the 3281 Å line is the stronger, but at high concentrations this line is so highly absorbed that the 3383 Å line appears to be the stronger. Because of this absorption effect, estimates of relative line intensities for a given element may be misleading.

Working curves are usually prepared from spectral data for synthetic mixtures containing the matrix element and added amounts of the various constituents sought in the analysis. It often happens that the matrix material contains an unknown amount (called a residuum) of some of these constituents; in such instances all apparent concentration values are in error by a constant amount. When this occurs, the spectral results may be corrected for the amount of the residuum.⁴⁵ This correction is made by a series of successive approximations. First, a working curve is made of log intensity against log concentration. When a residuum is present, this curve tends to become parallel to the log concentration axis at low concentrations. The best straight line is drawn through the points for the higher concentrations, and the amount of residuum is estimated from the magnitude of the departure of the lower concentration points from this line. Next, all concentrations are corrected by adding the estimated residual value, and the process is repeated. Two or three approximations usually suffice to bring all points onto a straight line. Finally, the correctness of the estimate is tested by using the working curve to determine, spectrographically, the amount of residuum in the pure matrix material. The value so obtained should agree with the value obtained by means of successive approximations. Failure to reach such agreement indicates that some other factor, such as background, must be taken into account. For example, a residuum correction on the uncorrected Al working curve of Figure 17, would give very erroneous values because of the effect of background. Whenever the line under examination is not absorbed the residuum can be determined in a single operation. After a working curve has been plotted as intensity ratio against concentration, a straight line is drawn through the higher concentration points. Next, another straight line parallel to the first is drawn through the origin; the displacement of the two lines on the concentration axis gives directly the amount of the residuum.

⁴⁵C. S. Duffendack and R. Wolfe, op. cit.

After a working curve has been accurately determined, the final form in which it is used depends upon the need for background correction in the process. No general statement can be made on this point. When a carbon supporting electrode is employed, it is usually well to correct for background; often, in the analysis of metal samples by a spark source, the background is negligible. When background corrections are not essential, it is advantageous to put concentration values instead of intensity ratios directly on the slide of the calculating board. When background corrections must be used, it is impossible to obtain concentration values by a single graphical operation because of the necessity for subtraction of intensities.

Internal Standards

An internal standard is used in practically every spectrographic analysis. The purpose of the standard is to correct for variations in the excitation conditions. None of the electrical sources used is absolutely reproducible; i.e., if exposures are made for separate portions of a given sample, the line densities of the several spectra obtained vary considerably. The chief reason for this variation is that the rate of vaporization of the sample material is beyond the control of the analyst. During the course of an exposure, the temperature of the source changes as the vapor atmosphere changes. Therefore, the probability of excitation for a vaporized atom will vary from time to time, since this probability depends upon the temperature of the source, to a certain extent. The material used for an internal standard should then have the following properties:

1. The internal standard line should have the same excitation potential as the analysis line, so that changes in temperature will affect both lines equally.
2. The internal standard should be vaporized at the same rate as the constituent sought in the analysis.
3. The internal standard should furnish suitable lines in the wave length region containing the analysis lines.

The internal standard should be added in such amounts that its line densities are approximately equal to those of the analysis lines. Since it is not always possible in practice to meet all the conditions mentioned the accuracy of the analysis depends upon the extent to which they are fulfilled. The best results

are obtained by spark excitation of metal samples, where the vaporization rate and the source temperature may be held relatively constant. Here, almost any matrix line of proper density and wave length can be used as standard. More difficulty is encountered in the analysis of solutions with the alternating current arc, for here the choice of a standard is often limited by the composition of the sample and by the solubility of the internal standard in the solution. In selecting a standard for an analysis of this latter type, a spectrum is first examined to determine qualitatively the impurity elements present, for no element present as impurity can be used as standard. Next, a wave length table is consulted for absent elements which give strong lines near the lines to be used for analysis. From among these elements those with compounds soluble in the sample solution are chosen. Test spectra are made with varying amounts of the chosen elements, in order to select proper concentration ranges for the standard, and to ascertain whether the spectrum of the standard has any lines which interfere with the analysis lines. This procedure often limits the choice of internal standards to a few substances. Among the most widely used internal standards are Mo and Co salts. These elements are chosen because they are of infrequent occurrence, they provide many suitable lines in the ultraviolet region, and they vaporize from the source at an average rate. Since Zn, Cd, Hg, and other similar elements have quite volatile salts, they are seldom used as internal standards. In the analysis of powders for which the d.c. arc must be used, it is often debatable whether an internal standard offers any advantages. The source often changes greatly in its characteristics during arcing, and unless the vaporization of the internal standard parallels that of the desired constituent, the standard does not serve its purpose. Moreover, proper mixing of the internal standard with the sample entails laborious grinding. Because of these difficulties, some workers omit the standard and merely arc weighed portions of the sample to complete vaporization.⁴⁶

Some spectroscopists have used background intensities in lieu of internal standards. This procedure is valid only where the background is excited concurrently with, but independently of, the analytical spectrum. Lundegårdh's work with flame excitation

⁴⁶M. Slavin, op. cit.

meets this condition. Here, the background comes from the burning acetylene, and changes in excitation conditions apparently are paralleled by changes in background intensity. In arcs, the background is due to cyanogen bands (when carbon electrodes are used), to incandescent particles of sample, and to band spectra from the sample material and from nitrogen. Since all of these factors except the band spectra from the sample may vary fortuitously, the background cannot be used as an internal standard.

Microphotometers

Non-recording, photoelectric microphotometers are almost universally used in spectrochemical analytical work. A microphotometer of this type should have the following characteristics:

1. The instrument should be free from stray light effects. If stray light reaches the photocell, all transmission values are too high.
2. The instrument should be sufficiently sensitive to give a full-scale deflection with a slit not over one-third the width of the line to be measured.
3. The scale reading must remain constant within one per cent over a period of at least ten minutes, so that I_0 readings need not be taken at more frequent intervals.
4. The galvanometer period should be short enough to permit a line density to be measured rapidly.
5. The construction should be such that the operator can quickly and accurately align the spectrum line with the slit.
6. There should be some convenient means to adjust the I_0 reading to a scale deflection of 100, so that galvanometer deflections are equal to per cent transmissions.
7. The galvanometer deflection throughout the range should be proportional to the light intensity transmitted.

An instrument fulfilling these requirements was constructed (see Figure 21). Its essential features are a low power light source which gives constant intensity and a slit arrangement which minimizes stray light. The plate is mounted on a screw-driven carriage, emulsion side down. The slit, usually measuring about 1.5×0.015 mm., is mounted beneath the plate, with a clearance of about 0.2 mm. The source is a straight-line, coiled filament headlight bulb operated at 6 volts and 5 amperes

by a constant power transformer. A reduced image of the filament is focussed at the slit. A photovoltaic cell is used in conjunction with a sensitive galvanometer to measure light intensity. The maximum photoelectric current is between 10^{-5} and 10^{-6} amperes. After a rough adjustment by varying the dimensions of the slit to bring the deflection to the approximate value desired, sensitivity is controlled by a resistance in series with the light. The plate is aligned by a mark on the slit jaws perpendicular to the center of the slit opening. After the spectrum has been aligned with the slit, the operator slowly moves the carriage by a lead screw, so that the line travels across the slit, while he observes the galvanometer deflection. With a little practice, it is easy to co-ordinate the movement of the carriage with the galvanometer period, so that the point of maximum density is not over-run. The rate of observation is about one line per minute, including a reading of the background transmission.

In all respects except convenience of alignment and speed of operation, the instrument described compares favorably with the commercial instruments available for tests. It is very stable, the I_0 value remaining constant for long periods after an initial warming up. Because of the low light intensities used and the isolation of the cell from the region of the lamp, the cell is very steady, and shows no appreciable drift with time. The amount of stray light entering the slit must be negligible, since the plate calibration curves remain linear up to densities well above 2.0. In this respect, this instrument is better than all but one of the commercial instruments tested. It gives the same density values as one subjective type of neutral wedge densitometer on the market. That its response is linear over the entire scale was proved by first measuring the transmission of an image for various slit widths, and then plotting the galvanometer deflection for the clear plate against the corresponding transmission through the image (Figure 20). The reproducibility of its readings is good; re-measurement of a whole plate seldom gives deviations greater than 0.01 density unit, except for lines of density greater than 1.5, where the error in reading the deflection is large.

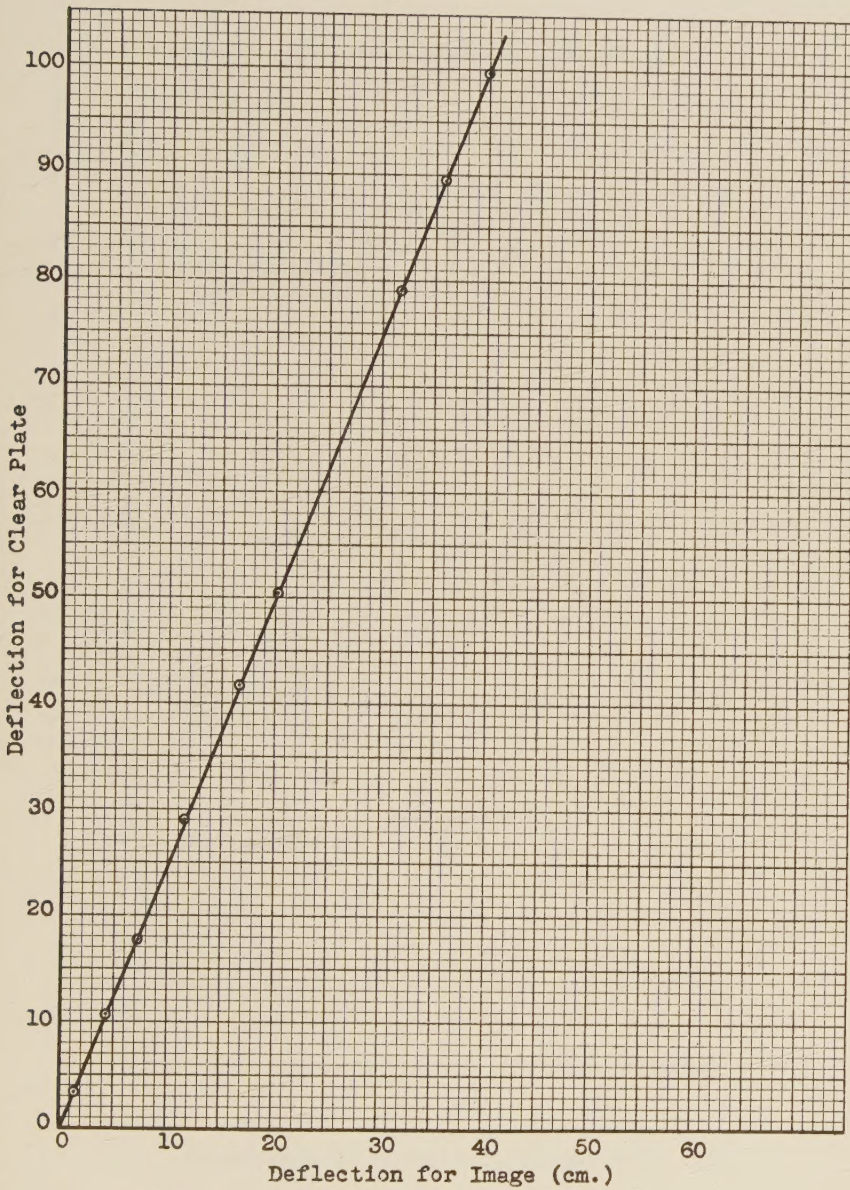


Fig. 20.--Linearity of photometer response

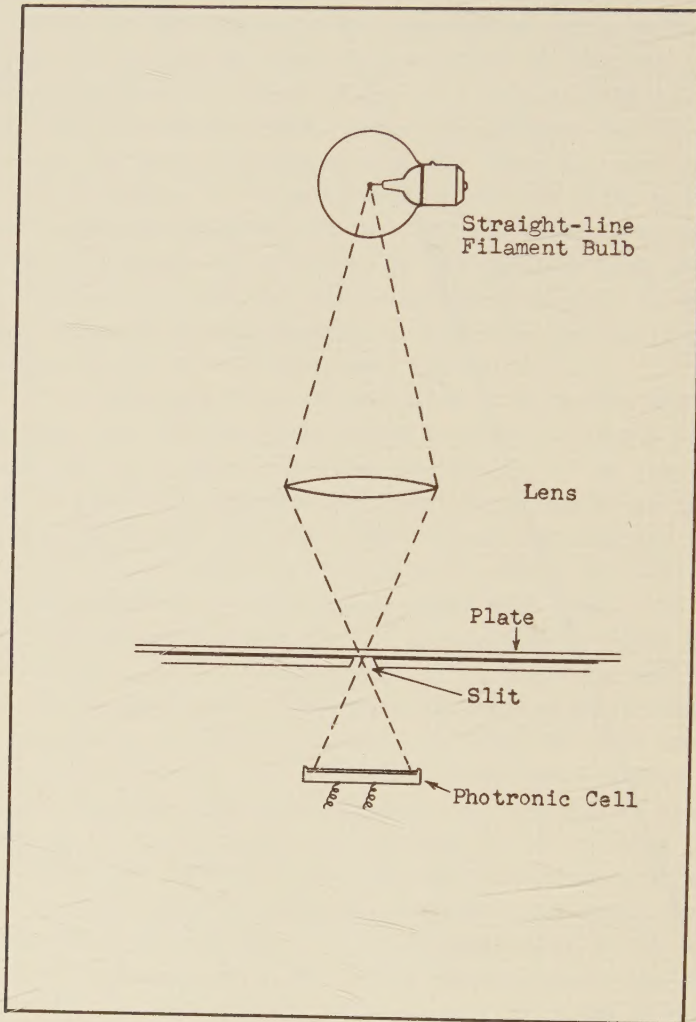


Fig. 21.--Schematic diagram of photometer

